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# CHARACTERISTICS AND PHOTOCHEMICAL REACTIVITY OF EMISSIONS

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# CHARACTERISTICS AND PHOTOCHEMICAL REACTIVITY OF EMISSIONS

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U.S. Bureau of Mines
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# THE ASSOCIATION OF AUTOMOTIVE FUEL COMPOSITION WITH EXHAUST REACTIVITY

by

Basil Dimitriades[1], B. H. Eccleston[2], G. P. Sturm, Jr.[3], and C. J. Raible[4]

## ABSTRACT

The association of automotive fuel composition with exhaust reactivity was studied in an experimental program that involved testing with different automotive engines and with gasolines of varied composition. Fuel composition was determined by gas chromatography. Exhaust reactivity was both estimated from detailed composition data and determined directly using a smog chamber. Results showed clearly the exhaust reactivity to increase with increasing levels of polyalkylbenzenes in the fuel. No other systematic patterns of high significance were detected in the association of exhaust reactivity with several broadly defined groups of fuel components. Evidence suggested, however, that such lack of relatability of exhaust reactivity and fuel composition was a result of inappropriate definition of fuel composition. For the purposes of this study, had it been possible, fuel composition should have been defined and expressed in terms of component groups such that the potential for exhaust reactivity would be the

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same within each group and different from group to group. Classification of fuel components in terms of the paraffins-olefins-aromatics groups does not meet the latter requirements. For appropriate classification of fuel components more information is needed on the combustion of hydrocarbons in the multicylinder internal combustion engine. Statistical analysis of the mass emissions data showed significant car and fuel effects on hydrocarbon, carbon monoxide, nitric oxide, total aldehydes, and formaldehyde emission levels and on total photochemical reactivity. Car-fuel interactions were not significant at the 90 pct level. Correlations were found between mass emission parameters and fuel composition.

## INTRODUCTION

Presently and undoubtedly for a large part of the decade of the 70's, a major portion of efforts in air pollution abatement has been and will continue to be directed to reducing emissions from automobiles. Of the objectionable automotive emissions, the hydrocarbons are prominent because of their principal role in photochemical smog formation. As a result, several control methods for hydrocarbons have been devised, some of which have already been put to use, others being further developed for use in the future. In most of these methods the approach is to use engine modification or accessory devices that would decrease the amount of hydrocarbon unburned in the primary combustion or convert the hydrocarbon emission into harmless product. This "device" or engine modification approach to emission control appears to have the potential for virtually complete elimination of the hydrocarbon emissions. A drawback, however, is the problem of retrofitting the automobiles already on the road.

Adjustment of fuel formula also could effect emission reduction either through reduction of emission levels or through emission modification resulting in less polluting material. While this "fuel optimization" approach may have only a modest potential for emission reduction per automobile, it has the advantage over the "device" approach that its application automatically encompasses all automobiles on the road.

The direction of the hydrocarbon control effort took a decisive turn with the recent setting of hydrocarbon emission standards for the 1975 automobiles (12).[5/] The stringency of these standards almost

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5/ Underlined numbers in parentheses refer to the list of references at the end of this report.

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eliminated for 1975 and 1976 model automobiles all control options except ones in which catalytic exhaust conversion devices are used. Such devices as have been developed, however, do not function effectively with fuels containing lead antiknock additives because of the poisoning effect of lead on the catalyst. Therefore, an inevitable part of the control measure necessary to meet the 1975 automobile standards is the reformulation of gasoline to provide the requisite octane quality without the use of lead antiknock additives. The extent of reformulation required appears to have been lessened by a reduction in compression ratio that was put into effect to lower the octane requirement of the engines of 1971 and later automobiles. However, this engine modification has also affected engine efficiency adversely, and one should reasonably expect that in the years to come the tendency will be toward higher engine compression ratio and hence toward gasolines made of higher octane quality hydrocarbons.

Besides the octane related change in fuel formula, additional fuel reformulation might become necessary as a result of new findings on the harmful effects of emissions. The present inventory of such effects is not necessarily complete. Chemical analysis of hydrocarbon combustion products, however advanced its methods may be, has not yet yielded identification of each and every component of the complex mixture of exhaust emissions. For example, with the exception of the lead additive, virtually no information exists on the fate of fuel additives in the combustion process. Evidence of heretofore unknown objectionable exhaust components or effects arising from the use of additives might raise a need for new or revised control techniques including further fuel reformulation.

It would therefore appear that, based on present projection of control needs, modification of gasoline fuel composition is to be anticipated. While the principal objective of such modification is to alter the combustion characteristics of the basic fuel hydrocarbon mixture, it is also desirable that the fuel change be in the direction toward minimum pollution from emissions. Achievement of the latter would require reliable comprehensive information on the association of fuel composition with pollution potential of emissions in order to provide some guidelines for fuel reformulation.

Existing information on the association of fuel composition with pollution potential of emissions lacks needed detail and at points is conflicting. Earlier studies conducted in this laboratory (3, 11) suggested that fuel aromatics may be associated with organic emissions of higher photochemical smog potential or reactivity. Results from other studies (6, 15) suggested that such an effect of fuel aromatics is either small or none. All these previous studies of the fuel composition factor

had the common inadequacy in that fuel composition was defined and expressed in terms of relative levels of broadly defined fuel component groups, namely, paraffins, olefins, aromatics. These classifications disregard possible effects of differing composition within each of these groups. Lacking evidence to the contrary, one cannot neglect the possibility that such effects may be as strong or stronger than those effects associated with each of the parent groups.

This report covers work done at the Bartlesville Energy Research Center in cooperation with the Environmental Protection Agency to further explore the association of fuel composition with pollution character of emissions. In view of the importance of the current issue regarding the effect of fuel aromatics on emission reactivity, this research was designed, in part, to provide information directly relevant to this issue. Further, attempts were made to determine more precisely the fuel/emission association by expressing fuel composition in terms of fuel component groups more narrowly defined than in the previous studies.

## EXPERIMENTAL DESIGN AND PROCEDURES

### Selection of Test Fuels

Ideally, in a study of fuel composition effects, test fuels would be selected so that the level of each of the 200 or so fuel components varies from fuel to fuel independently of the levels of other components. For example, for 200 components and two levels per component, a factorial experiment would require that about $2^{200}$ test fuels be used to determine main and interaction effects of the 200 components. If these effects vary with automobile, then additional tests will be required to determine the automobile effect. These requirements are clearly impractical, and some

simplification of the objectives must be made if the study is to entail a manageable effort.

Simplification can be accomplished by classifying the fuel components into a number of groups and by designing the study so as to determine the relative effects of these component groups--rather than of the 200 individual components. The success of such a simplification depends on whether the fuel component classification is consistent with the study's objective. Thus, if the objective is to relate fuel composition with pollution characteristics of fuel, then fuel composition ideally should be expressed in terms of component groups such that pollution characteristics would differ from group to group but would be similar within each group. The use of any other grouping scheme will result in a rating of the component groups used, based on their contributions to emission pollution, but will not reveal the full potential for fuel composition to influence pollution potential.

Available evidence suggests that fuel aromatics contribute to exhaust hydrocarbons mainly via unburned fuel and contribute only to a minor extent via combustion reactions that result in aromatic addition-products (9). This suggests that the reactivity of those exhaust hydrocarbons that originate from the fuel aromatics is determined mainly by the intrinsic reactivities of the aromatic hydrocarbons in the fuel. These reactivities are known to differ widely in value (8), and in a manner that justifies classification of fuel aromatics into three groups, in the following order of reactivity: polyalkylbenzenes > monoalkylbenzenes > benzene.

Relative to the aromatic fuel components, in typical automotive engine combustion the fuel paraffins are more readily burned or fragmented--fuel olefins even more easily oxidized. Therefore, the contribution of fuel paraffins and olefins to exhaust organics consists mainly of combustion

products rather than unburned fuel. Further, combustion products from fuel paraffins and olefins are distinctly different than those from aromatics in that they contain higher levels of reactive olefins and aldehydes and lower levels of unreactive acetylenes. Therefore, fuel paraffins, olefins, and presumably naphthenes also, should be differentiated from aromatics, as having distinctly different combustion and pollution characteristics.

For further classification of the fuel aliphatics, the supporting evidence is sketchy. Such evidence and reasonable speculation suggest: (a) Relative to straight chain fuel hydrocarbons, branched paraffins and olefins are more likely to yield exhaust olefins substituted at the double bond; such olefins are generally much more reactive than the straight chain ones. (b) Relative to branched olefins, branched paraffins yield higher levels of exhaust olefins (7). Finally, it is also likely that fuel aliphatics differ significantly in pollution characteristics even within each of the groups of branched paraffins, branched olefins, straight chain paraffins, and straight chain olefins, depending on molecular size and structure. While there is no experimental evidence directly applicable to this point, it has been shown that at least in pyrolysis of hydrocarbons, the composition of final products differs greatly with structure differing within the group of branched paraffins (14).

Thus the available information justifies classification of fuel components on the basis of their contribution to exhaust pollution characteristics in at least the following detail: Benzene, monoalkylbenzenes, polyalkylbenzenes, olefins, branched paraffins, and straight chain paraffins. Further breakdown or an entirely different classification scheme based on molecular structure, may be shown to be more appropriate if and

when more information is generated on degradation patterns in automotive combustion of hydrocarbons.

The preceding considerations led to the design of 10 test fuels (fuels 12 to 21, table 1) that contained varying levels of benzene, monoalkylbenzenes, polyalkylbenzenes, n-paraffins, isoparaffins, cycloparaffins, n-butane, and olefins. Fuels listed as 1 to 9 in table 1 were test fuels used in a separate study of commercial gasolines (92-94-RON) marketed for use with the 1971 model year automobiles. Data from that fuel-evaluation program were found to be relevant to the objectives of the fuel composition effect study; therefore, data from both studies were pooled.

Fuels 10 and 11 (table 1) were commercial unleaded premium gasolines with unusually high levels of aromatics. These two fuels were also included in order to provide additional data on the effect of fuel aromatics on emission reactivity. Fuels 22 to 25 (table 1) were those used in an earlier Bureau of Mines study (3, 11) in which fuel aromatics were shown to have a strong effect on emission reactivity; these fuels were reused in this study in order that additional information could be added to that from which previous conclusions were drawn.

In addition to the full-boiling range gasolines, a few simple hydrocarbon fuels (table 2) were also used in experiments in the small two-cylinder engine. The purpose of this work, as discussed later, was to gain information on the degree to which pollution characteristics of the various specific fuel hydrocarbons vary.

## Tests Using Full-Boiling Range Gasolines

The gasolines were studied using 11 automobiles (table 3) selected to represent typical, high production, late models.

Engines of automobiles in the test program were adjusted according to manufacturer's specifications. In the first phase of this program, automobiles 1 through 9 were used in tests with eight fuels (fuels 1, 4-10, table 1). Each automobile was operated at 85° F ambient temperature following a 22.9 minute engine duty cycle (Federal cycle for 1972 automobiles and later (13)). Limited testing was also conducted at 45° and 20° F ambient temperatures. Samples of exhaust in mixture with air were drawn throughout the engine test as prescribed in Federal test procedures for 1972 automobiles (13).

In the second phase of the program, automobiles 5, 6, 7, 9, and 10 were used to test fuels 12 through 21. Each automobile was operated at 75° F ambient temperature following the same engine cycle as in the first phase. Exhaust was sampled as prescribed in Federal test procedures for 1975 automobiles (12); that is, three samples were collected to provide sample of (1) exhaust in the cold start part of the cycle, (2) in the remaining stabilized part, and (3) in the hot start part, respectively. In both phases of this study, exhaust was analyzed for individual hydrocarbons (4), total hydrocarbon by flame ionization detection (FID), total aldehydes (10), formaldehyde (1), oxides of nitrogen ($NO_x$) by nondispersive infrared (NDIR), carbon monoxide (CO) by NDIR, and carbon dioxide ($CO_2$) by NDIR. The data from these tests were used to associate fuel composition with exhaust hydrocarbon composition (without reference to experimentally observed reactivity or smog potential).

Note that while the two phases of the program had somewhat different specific objectives and experimental conditions, their respective data, being relevant to the issue of fuel/emission association, were pooled together. For such pooling, analytical data from the three exhaust samples

per test in the second phase were combined mathematically to yield data comparable to those obtained in the first phase. Also, the difference in test temperature between the two phases (85° F versus 75° F) was judged to have no significant effect on the fuel/emission association and was, therefore, ignored.

This experimental program that involved the eleven automobiles was expected to provide data suitable and adequate to establish the association of fuel composition with exhaust hydrocarbon composition, but not with exhaust hydrocarbon reactivity. The latter limitation was because the exhaust samples from this program contained relatively high levels of $NO_x$ that prohibited experimental measurement of exhaust hydrocarbon reactivity in photochemical smog chambers (2). For such measurement to be feasible, the hydrocarbon/$NO_x$ ratio in exhaust must be higher than 3:1 (ppmC:ppm) (2); such a condition can be realized only when the automotive engine operates under richer than normal air-fuel (A/F) conditions. Alternative methods for estimating exhaust hydrocarbon reactivity from exhaust hydrocarbon composition have been shown to be much less reliable than direct experimental measurement (3). This consideration led to designing a separate program to study the association of fuel composition with exhaust hydrocarbon reactivity.

### Smog Chamber Tests Using Full-Boiling Range Gasolines

In the smog chamber program the experimental fuels (fuels 1-25, table 1) were studied using an automobile that was operated fuel-rich in order to yield exhaust with high hydrocarbon-to-$NO_x$ ratio as required for smog chamber examination. Exhaust samples in this program were analyzed as in fleet testing and were also examined in a smog chamber for photochemical reactivity. For reactivity measurement, exhaust at the

initial levels of 6 ppmC hydrocarbon, 0.9 ppm NO, and 0.1 ppm $NO_2$ was irradiated in a smog chamber following procedures described in the literature (2).

Because the test automobile in the smog chamber program was operated fuel-rich, the question was raised whether this perturbation in an engine operation condition would invalidate the findings of the smog chamber program. To investigate this, additional testing was conducted in which one automobile and one small two-cylinder engine were operated under varied A/F conditions, using gasolines as well as the simple hydrocarbon fuels.

## Testing of Simple Hydrocarbon Fuels

Results from the gasoline testing program described in the preceding sections indicated a need for information on the automotive combustion characteristics of specific hydrocarbon types. More specifically, such information was needed to serve the following purposes:

A. To demonstrate the degree to which reactivity of exhaust from various hydrocarbons varies with hydrocarbon structure.

B. To provide guidelines for classifying hydrocarbons into groups such that the potential for exhaust reactivity would be different from group to group but uniform within each group.

The experimental program that was run was undertaken and designed with the first purpose in mind; to serve the second purpose, a much larger research effort would be necessary.

Fourteen prominent fuel compounds (table 2) were chosen to represent several classes of hydrocarbons in gasoline fuels. The fuels were run in a two-cylinder water-cooled engine (Onan) at three A/F equivalence ratios--0.75, 1.0, 1.1. For all tests, the engine was operated at 1,800 rpm

(1,800 rated speed) and at one-fifth full load. Exhaust was sampled and analyzed for individual hydrocarbons by gas liquid chromatography (GLC), total hydrocarbon, formaldehyde, total aldehydes, $NO_x$, CO, and $CO_2$. Exhaust samples from the rich operation mode were also irradiated in the smog chamber for measurement of the photochemical reactivity. Duplicated chamber runs were conducted with initial exhaust level at 6.0 ppmC hydrocarbon, 0.9 ppm NO, and 0.1 ppm $NO_2$.

## RESULTS - DISCUSSION

### Tests Using Full-Boiling Range Gasolines

Results from tests with the eleven automobiles are given in tables 4 and 5. The tabulated data are for emission rates of exhaust hydrocarbon, CO, $NO_x$, total aldehydes, and for hydrocarbon reactivities calculated from hydrocarbon compositions.

These results were analyzed statistically for correlations between fuel composition and exhaust emissions. Such correlations, if present, were to be interpreted to provide a measure of the relative contributions of fuel hydrocarbons to exhaust emissions. Correlations with exhaust emission rates are described and discussed in appendix A. The remainder of this section deals with the correlation of fuel composition with concentrations of reactive organics (hydrocarbons and aldehydes) in exhaust.

The exhaust parameters used in this correlation analysis included calculated reactivities, formaldehyde, total aldehydes, and several olefins and aromatics that are known to contribute significantly to exhaust reactivity. Varied schemes and combinations of hydrocarbon class and subclass division and groupings were used as parameters of fuel composition. Thus, in one attempt exhaust composition was correlated with fuel composition

expressed in terms of paraffin, olefin, and aromatic. In other correlation models, fuel composition was expressed in terms of more narrowly defined component groups. Correlation analysis was applied upon data from each automobile separately. Using such data, the fuel/exhaust correlations were not obscured by car effects or car/fuel interaction effects. Such effects, while undesirable in the correlation analysis, are nevertheless of interest, and were explored in a separate statistical analysis.

The correlation models that were used and results from the correlation analysis are illustrated[6/] by information summarized in table 6 for car 5.

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6/ Correlations were obtained from statistical analysis of data from each car examined individually. Results were similar, car-to-car, and the following discussion is to be construed as representing the typical case.

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Degree of correlation is represented by the value of $R_{SQ}$ in table 6, a high $R_{SQ}$ value representing a high degree of correlation. From the data of table 6, apparently better fuel/exhaust correlations are generally obtained when fuel composition is expressed in terms of a more detailed classification of the fuel components. For example, breaking the aromatic portion of the fuel into benzene, monoalkylbenzenes, and polyalkylbenzenes (model II) gave a fuel/exhaust correlation that was improved over that obtained when the total of aromatics is used as one fuel component (model I). This suggests that the source of a reactive exhaust organic is associated with a narrowly defined group or even an individual fuel component rather than with a broadly defined class of fuel hydrocarbons. This is more clearly illustrated by the correlation results for exhaust toluene

and xylenes (see table 6). Levels of toluene and xylenes in exhaust were found to correlate much better with fuel composition when fuel aromatics were broken into benzene, monoalkylbenzenes (mostly toluene) and polyalkylbenzenes (mostly xylenes), with $R_{SQ}$ values increasing from 0.66 and 0.41 to 0.94 and 0.80, respectively, for car 5. Evidently this was so because exhaust toluene and xylenes originate almost entirely from the toluene and xylenes (in fuel) and not from all fuel aromatics. In line with this reasoning, the rather poor correlations of exhaust olefins with fuel composition might be due to inappropriate grouping of fuel components. If so, then better correlation could be obtained if fuel components were classified into groups such that yield in exhaust olefins would be uniform within each group. Another difficulty in the correlations for exhaust olefins is the rather narrow ranges in yields as indicated by the standard deviations about the means as seen in table 6. For example, the standard deviation for ethylene is about 20 pct of the mean value as compared to about 60 pct for toluene. Also, for low yield components such as 2-methylbutene-2, the experimental error in the concentration measurement may be important.

The main conclusion reached in consideration of the statistical data thus far is that better correlations of fuel composition with exhaust composition and calculated reactivity are obtained when fuel composition is expressed in more detail than is provided by the simple classification into paraffins, olefins, and aromatics. This statistical conclusion is interpreted to mean that pollu-tion characteristics of fuel components vary considerably within the class of aromatics, as predicted by theory, and possibly within the paraffin and olefin classes also. Further interpretation of these statistical results--e.g., to identify or quantitatively associate

source of an exhaust hydrocarbon with a specific group of fuel components--is not valid. Qualitative associations, however, might have significance. Thus, we examined the associations between calculated (Jackson) exhaust reactivity and the levels, in fuel, of aromatics, polyalkylbenzenes, olefins, paraffins, and isoparaffins. Systematic patterns were obtained only in the reactivity-versus-fuel polyalkylbenzenes and reactivity-versus-fuel olefin plots (figures 1 and 2), and even then the dependencies implied,

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FIGURE 1. - Correlation of Calculated Exhaust Reactivities With Polyalkylbenzene Levels in Fuel.

FIGURE 2. - Correlation of Calculated Exhaust Reactivities With Olefin Levels in Fuel.

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although real, were nevertheless weak. Such failure to uncover strong dependence of exhaust reactivity on a specific group of fuel components may have been caused by the fact that the fuel component groups that were considered were inappropriately defined.

Since the analysis discussed thus far involved data from one automobile only, the question was raised whether the conclusions reached are valid for other automobiles also. It was also questioned whether whatever car effect exists is caused solely by air/fuel variation from car to car. To answer these questions, a statistical analysis was applied upon the data obtained in the second phase of the fleet testing program when A/F data were taken for all test cars. The statistical method used was similar to the one used in the fuel/exhaust correlation. Specifically, exhaust composition and calculated reactivity were again correlated with the fuel composition, except that this time data from five automobiles were pooled

and the correlation models used were:

I. $(\text{Exh. Component})_i = F\ (\text{fuel composition})$

II. $(\text{Exh. Component})_i = F\ (\text{fuel composition}) + a_1c_1 + a_2c_2 + a_3c_3 + a_4c_4$

III. $(\text{Exh. Component})_i = F\ (\text{fuel composition}) + a_1\ (A/F)$

where

F (fuel composition): Function of fuel composition

$a_1c_1$, $a_2c_2$, $a_3c_3$, $a_4c_4$: Terms representing contributions of cars 6, 7, 9, and 10, to component i in the exhaust relative to that from car 5.

$a_1\ (A/F)$ : Term representing "contribution" of A/F to exhaust component i.

The experimental data were fitted to these statistical models and results were used to determine whether inclusion of the car or A/F variables improved the fuel/exhaust correlation. Results, summarized in table 7, show that inclusion of the car variables improved correlation substantially, suggesting, thus, presence of a strong car effect. Use of the A/F variable in lieu of the car variables had a much smaller effect, suggesting, thus, that the car effect was not a result of variation in average-over-the-engine-test A/F.

Presence of "car effect" is interpreted to mean that the same fuel may yield different exhaust hydrocarbon mixtures in different automobiles. This raises the question, then, whether a change in fuel composition would have different effects on the exhaust from different automobiles. Such a nonuniform fuel effect, in the language of statistics, is referred to as car/fuel interaction effect and is represented by the car-fuel product terms in the following statistical model:

$(\text{Exh. component})_i = a_1 \times \text{Fuel}_1 + \ldots + c_1 \times \text{Car}_1 + \ldots + k_1 \text{ Fuel}_1 \times \text{car}_1 + \ldots$

Statistical analysis of the data from the first phase of the multiple-vehicle program showed that the car/fuel interaction effect was small, suggesting, that a change in fuel composition would have equal effects on exhaust from different automobiles. This finding is useful in that it suggests that in studying the effect of fuel composition on hydrocarbon emissions, use of a large number of test automobiles may be unnecessary.

## Smog Chamber Program

Results from the smog chamber program are given in table 8. The most significant observations from these results are that the exhaust samples tested did not show large differences in reactivity in spite of the great diversity in fuel composition. In fact, from plots of exhaust reactivity against fuel aromatics (figure 3)[7/], the dependence of reactivity on fuel

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FIGURE 3. - Correlation of Observed Exhaust Reactivity With Total Aromatic Levels in Fuel.

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7/ Exhaust reactivity in this and following figures is expressed in units of molar propylene equivalents; that is, in units of reactivity of an equimolar concentration of propylene.

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aromatics did not seem to be as strong as previous studies in this laboratory had suggested (figure 4, dark circles). In view of the importance of the

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FIGURE 4. - Correlation of Exhaust Reactivities With Total Aromatic Levels in Fuel. (Previous Bureau of Mines Study.)

issue regarding the effect of fuel aromatics on exhaust reactivity, the data from this program were scrutinized in searching for information relevant to this issue. Thus, we explored the possibility, suggested by the multiple-car tests that exhaust reactivity depends on levels of some, but not the total of all, fuel aromatics. Results showed that exhaust reactivity, indeed, appears to be more strongly dependent on polyalkylbenzenes (figure 5), than on total aromatics in fuel. This finding, consistent with the

FIGURE 5. - Correlation of Observed Exhaust Reactivities With Polyalkylbenzene Levels in Fuel.

fleet testing results from the multi-vehicle tests probably establishes the relatively high pollution potential of polyalkylbenzenes in fuel. However, the effect of the polyalkylbenzenes on exhaust reactivity does not alone explain the unusually large differences in exhaust reactivity that were observed for some of the fuels in the earlier Bureau of Mines study (3).

In attempting to understand the differences in results between this and the earlier Bureau of Mines studies regarding effect of fuel aromatics on exhaust reactivity, we explored the possibility that experimental error may account for part or all of the difference in question. To this end, we fitted the data from this study to the exhaust reactivity--exhaust composition correlation equation developed in the earlier study. Figure 6

FIGURE 6. - Correlation of Observed and Calculated (Jackson Scale) Exhaust $R_{NO_2}$ Reactivities.

shows the curve depicting that correlation equation along with the scatter

boundaries and the correlation data (dots) obtained in the present study. The excellent agreement between the correlation points of the two studies suggests that the quality of experimental data (smog chamber reactivity and chromatographic analysis data on exhaust hydrocarbons) was about the same for the two studies. This would discredit experimental error as the sole cause of the difference in results between the earlier and the present studies. Finally, to determine whether differences in test conditions can account for these differences, the fuels of the earlier Bureau of Mines study (fuels 22-25, table 1) were tested again; this time using the experimental automobile and conditions of the present study. Retesting included chromatographic analysis of fuels since the present fuel samples were taken from a new batch that might differ somewhat in composition from the fuel batch used in the earlier study. Results of the reactivity observations given in table 9, did show a trend of increasing reactivity with increasing levels of fuel aromatics (see figure 4, crosses) but this trend was not as strong as that that was observed in the earlier study (figure 4, dots). It was, therefore, deduced that the differences in results between this and the earlier fuel studies were caused, partly at least, by differences in test conditions.

In attempts to associate exhaust reactivity with nonaromatic fuel components, reactivities were plotted versus total olefins, internal olefins, n-paraffins, and isoparaffins in fuel for constant total aromatic or total polyalkylbenzenes. With one exception, no systematic patterns could be observed in these plots, suggesting that composition differences within the groups of olefins, n-paraffins, and isoparaffins, are probably causing some differences in exhaust reactivity. The exception was the apparent correlation between peroxypropionyl nitrate (PPN) yields in the irradiated

exhaust and the level of olefins in the fuel. Note that peroxyacetyl nitrate (PAN) yields did not show the same trend. This might suggest that PPN results mainly from fuel olefins surviving in the exhaust, rather than from olefins that result from the combustion process and yield primarily PAN.

An alternative approach to relating exhaust reactivity with fuel composition is through intermediate correlation with exhaust composition. Application of this approach was illustrated in the American Petroleum Institute study (of the effect of fuel composition on exhaust reactivity) (3). Briefly, the approach entails statistical treatment of exhaust composition and exhaust reactivity data to develop a reactivity-composition correlation equation. Using such an equation upon the data from the multiple-vehicle tests, exhaust reactivities are obtained from exhaust compositions and are subsequently correlated with fuel composition. In the present study this approach did not appear promising at first, primarily because exhaust reactivity did not correlate well with exhaust composition. Part A of figure 7 depicts this correlation using as measure of exhaust

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FIGURE 7. - Correlation of Observed Exhaust $R_{NO_2}$ Reactivities With Calculated Reactivities by Jackson and Bureau of Mines Scales.

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composition the "linear summation reactivity" value obtained from exhaust composition and Jackson specific reactivity data (8). Part B of figure 7 depicts the same correlation, except that here linear summation reactivity values were calculated from Bureau of Mines specific reactivities as shown in table 10, rather than Jackson reactivities. Use of the specific

reactivities shown in this table did improve the correlation but not to the point of providing a usable correlation equation. This lack of strong correlation in the data of this study was attributed to the narrow range within which the correlation variables (exhaust reactivity and exhaust composition) were included.

The analysis of the smog chamber data thus far points to the same conclusion that was reached in tests with the eleven automobiles, namely: Differences in reactivity among exhausts from different fuels are not caused solely by differences in relative levels of paraffins, olefins, and aromatics in fuel; differences in composition within each of these hydrocarbon classes are also a factor.

This conclusion led to the idea of attempting to correlate exhaust reactivity with fuel composition expressed in terms of individual component--rather than component group--data. The concept here entails development of a "fuel reactivity scale", that is, a rating system by which each fuel component would be rated according to its contribution to exhaust reactivity. Given those ratings or "specific reactivities" ($r_i$), and the mole fractions of the individual fuel components ($x_i$), exhaust reactivity ($R_{exh}^{calc}$) could then be calculated using the equation

$$R_{exh}^{calc} = \Sigma x_i r_i$$

The success of this method for correlating exhaust reactivity with fuel composition would be measured by the extent of agreement between the calculated ($R_{exh}^{calc}$) and observed ($R_{exh}^{obs}$) exhaust reactivity values.

In order to use this correlation method upon the data of this study, first specific reactivity values had to be assigned to the various fuel components. Several alternative sets of such assignments were made based

on speculation and on the limited information available regarding automotive combustion of hydrocarbons. The set of assignments that gave the best predictions of exhaust rate-of-$NO_2$-formation reactivity was as follows: Except for paraffins, each fuel hydrocarbon was given a specific reactivity value equal to that assigned by Jackson (8); paraffins were given reactivity values equal to twice the corresponding Jackson value. The rationale of these assignments is based on the fact that reactive exhaust organics consist mainly of unburned fuel and of products from cracking of the aliphatic fuel components. Following these specific reactivity assignments, exhaust reactivity was calculated, and resultant values were compared to those for observed exhaust reactivity. Results are shown in figure 8. The

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FIGURE 8. - Correlation of Observed Exhaust Reactivities With Calculated "Fuel" Reactivities.

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correlation appears to be good despite the speculative character of the specific reactivity assignments made. This verifies the advantage of expressing fuel composition in terms of individual component data rather than in terms of broadly defined fuel component groups. Interestingly, exhaust reactivity did not correlate as well with exhaust composition (see Part A of figure 7) as it did with fuel composition (figure 8). This is probably due to relatively large experimental errors in the chromatographic measurement of exhaust composition; error in chromatographic measurement of fuel composition is much smaller.

## Influence of Engine Air-Fuel Ratio on Correlation Results

Operating the test automobile used in the smog chamber program with fuel-enriched A/F raised questions regarding validity of results and

prompted a brief investigation of the effect of A/F on reactivity of exhaust emissions. Data for this investigation were obtained both in the simple hydrocarbon fuel testing program of this study and in another study in which a 1963 Chevrolet engine, 283 cu-in-displacement (CID), was operated under varied A/F conditions using gasoline fuels of various compositions. The data from the simple fuel tests (discussed also in the following section of this report), plotted in figure 9, showed the A/F to have a nonuniform

FIGURE 9. - Calculated $R_{NO_2}$ Reactivities of Exhaust From Simple Hydrocarbon Fuels Used Under Varied A/F Conditions.

effect on exhaust reactivity. Thus, with the paraffin fuels, the A/F effect was strong in the fuel-rich region and weak in the fuel-lean region, and its magnitude varied only moderately from fuel to fuel. With the aromatic fuels, the A/F effect was generally weak throughout the A/F range used. With the olefin fuels, the A/F effect was strong, and its magnitude varied considerably from fuel to fuel. These data suggest that with gasolines the A/F effect may vary in magnitude from fuel to fuel depending on aromatic and olefin content.

More direct information on the effect of A/F on gasoline exhaust reactivity was provided by the tests with the Chevrolet engine. Results from these tests are shown in figure 10. These results indicate that

FIGURE 10. - Calculated $R_{NO_2}$ Reactivities of Exhaust From Gasoline Fuels Used Under Varied Air-Fuel Ratio Conditions.

although changes in A/F affect exhaust reactivity, the changes affect the exhaust from different fuels in the same manner, preserving the relative order of their reactivities and therefore, preserving relative fuel effects on exhaust reactivity. This finding, in turn, suggests that fuel enrichment of the A/F, necessary for acceptable $HC/NO_x$ in exhausts produced for the smog chamber study, does not invalidate the conclusions from the study regarding the effect of fuel composition on exhaust reactivity.

## Automotive Combustion of Simple Hydrocarbon Fuels

Results from the simple hydrocarbon fuel tests are given in table 11. Observed exhaust reactivity data are summarized in table 12. Note that these data represent specific reactivity of exhaust, that is, reactivity per mole of exhaust hydrocarbon, and they should be looked at solely as indicative of the nature of the exhaust organics that originate from the various fuel components. Data for the n-heptane and hexene-1 fuels could not be obtained directly because these hydrocarbons, having extremely low octane number, could not be used alone. The exhaust reactivity values listed in table 12 for these two hydrocarbons represent only gross estimates. They were obtained from comparison of data from the heptane and hexene-1 mixtures with aromatics versus data from the aromatics alone.

Regarding the main objective of these tests, the data of table 12 show that fuel hydrocarbons of varying structure yield exhaust of widely varying reactivity. The data support deductions drawn from the other segments of this study that for purposes of predicting exhaust reactivity, the simple classification of fuel hydrocarbons into paraffins, olefins, and aromatics is clearly inadequate. Further, the data confirms that structural differences within each of the constituent groups have equal

or greater effect on exhaust reactivity than do the differences group-to-group. Although the present data are not sufficient to permit a fully adequate classification of fuel hydrocarbons, they nevertheless are suggestive of certain trends. Thus, normal paraffins appear to yield exhaust of relatively low reactivity, whereas cycloparaffin fuel yields exhaust considerably more reactive. Isoparaffin fuels may very considerably in (exhaust) reactivity, evidently, depending on their molecular structures. Olefins of various molecular structure seem to yield exhaust of widely varying $R_{NO_2}$-reactivity but of almost constant ozone-yield reactivity. Aromatic fuels of differing aromatic make-up also yield exhaust of widely varied reactivity, the polyalkylbenzenes appearing to yield exhaust that is considerably more reactive than the exhaust produced from monoalkylbenzenes and benzene. The data from the tests with the n-heptane mixtures (table 12) suggest also that the pollution potentials of the various hydrocarbons are preserved when these hydrocarbons are used in mixture with others; evidently there are no strong synergistic effects in this respect.

Another interesting observation from these data pertains to the degree of agreement between observed and calculated reactivity values for exhaust from simple fuels. Figure 11 illustrates the degree of agreement between

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FIGURE 11. - Correlation of Observed and Calculated $R_{NO_2}$ Reactivities of Exhaust From Simple Hydrocarbon Fuels.

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observed $R_{NO_2}$-reactivity of exhaust and reactivity calculated from GLC-composition of exhaust and the Jackson reactivity scale (8). Observed reactivity values are considerably higher than the calculated ones. Note that the calculated reactivity value does not include the reactivity

contribution of formaldehyde and a portion of the contributions of the heavier aldehydes. This is because the flame ionization detector used in the GLC method does not respond to formaldehyde and has relatively low response to the heavier aldehydes (5). Nevertheless, levels of aldehydes, as measured by the chromatropic acid and MBTH methods, are too low (see table 11) to affect noticeably the difference between observed and calculated reactivities.

These differences between observed and calculated reactivities have been noticed previously (3); however, the present data provide a somewhat more precise definition of this problem. Thus, for exhaust from aromatic fuels and for relatively more reactive exhaust the difference between observed and calculated reactivities is larger than for the rest of the exhaust samples of this study. This explains the large amount of scatter observed in correlations of observed and calculated reactivities of exhaust from fuels of varying aromatic contents (e.g. see figure 7). The cause of this problem is not known. Nevertheless, based on experiences in this laboratory, these investigators speculated that the higher-than-expected reactivity of exhaust is caused, partly at least, by reactive exhaust organics that have been totally missed or misidentified by sampling and the chromatographic method of exhaust analysis (5). The data from the present study underscore once again the unreliability of the "calculation" method as it is often used to estimate reactivity of exhaust emissions.

## SUMMARY AND CONCLUSIONS

In efforts to associate automotive fuel composition with reactivity of exhaust emissions, a number of fuels of varied composition were tested using several automobiles operated with standard engine adjustments. The

one investigative approach, exhaust reactivity, was calculated using a reactivity scale and exhaust composition data. Such calculated exhaust reactivity was then statistically correlated with fuel composition expressed using each of several different component classification schemes. Results showed that correlations were improved when compositional detail was added to the simple classification as paraffins, olefins, and aromatics. A similar conclusion was reached when levels of selected reactive exhaust components were statistically correlated with fuel composition. Further, from the fuel component groups considered, the group of polyalkylbenzenes was found to be the one that correlated best with calculated exhaust reactivity. The broader group of aromatics showed a weak correlation.

By an alternate investigative approach, fuel composition was correlated to exhaust reactivity that, instead of having been calculated, was measured experimentally using a smog chamber. For these smog chamber measurements the experimental fuels were tested using one automobile that was operated fuel-rich in order to yield exhaust with sufficiently high $HC/NO_x$ ratio. Evidence was obtained in parallel to show that such operation of the test engine did not invalidate the findings from this smog chamber program. Findings in the smog chamber tests were essentially in agreement with those of the multiple-car tests. The failure to observe a strong effect of aromatics on exhaust reactivity contradicted indications from a previous study in this laboratory. In order to resolve or reduce the uncertainty posed by the differences, fuels used in the earlier study were retested under conditions of the present study. Results from this retesting did not provide a satisfactory explanation of the contradiction and the difference in question was attributed to differences in experimental conditions between the two studies.

The polyalkylbenzenes were the only fuel component group that were indicated by the correlations positively to have an influence on exhaust reactivity. Other components are, nonetheless, believed to have such an effect. Lack of strong correlation between exhaust reactivity and other fuel component groups, such as paraffins, isoparaffins, olefins, and internal olefins, was attributed to inappropriate definition of these groups. It is now indicated that to associate composition and exhaust reactivity, fuel composition should be expressed either (1) in terms of individual components or (2) in terms of component groups such that the potential for exhaust reactivity would be the same within each group and different from group-to-group. Classification of fuel components in terms of the paraffins-olefins-aromatics groups apparently did not meet the latter requirement. This was verified in tests with single component hydrocarbon fuels that showed the potential for exhaust reactivity varies widely within each of the fuel component groups of paraffins, olefins, and aromatics. For appropriate classification of fuel components considerably more information is needed on the fuel-derived products of combustion from automotive engines. Given such information prediction of exhaust reactivity can be made using either (1) a correlation derived from experimental data, or (2) by the application of product-yield reactivity values to the fuel constituents--individually and/or suitably grouped. The latter approach (2) was tested using experimental data generated in the study. Using some gross assumptions, fuel components were assigned reactivity ratings and exhaust reactivity predictions were made based on these fuel component reactivities and mole fractions. Such predicted exhaust reactivity values were found to correlate well with those for observed reactivity.

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TABLE 1. - Experimental fuels used in the gasoline fuel test program

| Specifications | Fuel No. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Grade | Regular | Regular | Regular | Regular | Regular | Regular | Special | Special |
| RVP | 10.4 | 9.1 | 11.3 | 10.2 | 9.3 | 8.3 | 10.1 | 11.5 |
| Specific gravity | .725 | .747 | .746 | .747 | .731 | .725 | .707 | .755 |
| TEL, ml/gal | 0 | 0 | .35 | .34 | 1.90 | 1.80 | 0 | 0 |
| Research octane No. | 1/ 91 | 1/ 91 | 1/ 94 | 1/ 91 | 1/ 94 | 1/ 94 | 92 | 97 |
| Distillation, °F: | | | | | | | | |
| IBP | 88 | 96 | 100 | 106 | 105 | 92 | 88 | 88 |
| 10 percent | 122 | 134 | 136 | 126 | 125 | 128 | 122 | 110 |
| 50 percent | 210 | 234 | 240 | 220 | 199 | 198 | 218 | 215 |
| 90 percent | 304 | 340 | 376 | 309 | 324 | 308 | 300 | 308 |
| End | 374 | 404 | 418 | 435 | 415 | 392 | 382 | 378 |
| GLC composition, mole percent: | | | | | | | | |
| Paraffin | 67.7 | 60.5 | 69.1 | 58.8 | 64.2 | 67.0 | 81.0 | 48.2 |
| Olefin | 9.0 | 7.6 | 6.7 | 13.0 | 10.2 | 6.2 | 4.5 | 6.6 |
| Aromatic | 23.3 | 31.9 | 24.2 | 28.2 | 25.6 | 26.8 | 14.6 | 45.2 |
| Monoalkylbenzenes | 8.8 | 10.0 | 3.3 | 6.8 | 6.6 | 9.1 | 4.3 | 14.3 |
| Polyalkylbenzenes | 12.1 | 20.6 | 20.3 | 20.2 | 18.3 | 15.3 | 8.2 | 23.9 |
| n-Paraffins | 21.4 | 16.3 | 21.5 | 18.1 | 22.9 | 19.5 | 21.3 | 23.6 |
| Isoparaffins | 41.4 | 38.9 | 37.6 | 34.9 | 36.1 | 42.4 | 58.0 | 22.2 |
| Cycloparaffin | 4.8 | 5.3 | 10.0 | 5.8 | 5.1 | 5.1 | 1.6 | 2.4 |

1/ Estimates of RON from fuel specified.

TABLE 1. - Experimental fuels used in the gasoline fuel test program (Cont'd)

| Specifications | Fuel No. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
| Grade | Special | Premium | Premium | Special | Special | Special | Special | Special |
| RVP | 10.0 | 12.8 | 10.1 | 8.4 | 7.7 | 7.9 | 7.7 | 7.5 |
| Specific gravity | .738 | .755 | .771 | .731 | .731 | .731 | .762 | .712 |
| TEL, ml/gal | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Research octane No. | 95 | 100 1/ | 100 1/ | 92 | 92 | 93 | 95 | 94 |
| Distillation, °F: | | | | | | | | |
| IBP | 86 | 86 | 92 | 108 | 100 | 102 | 106 | 108 |
| 10 percent | 118 | 120 | 140 | 136 | 138 | 134 | 146 | 136 |
| 50 percent | 230 | 230 | 240 | 186 | 186 | 202 | 226 | 168 |
| 90 percent | 308 | 326 | 318 | 284 | 254 | 292 | 282 | 246 |
| End | 366 | 364 | 378 | 380 | 382 | 378 | 350 | 288 |
| GLC composition, mole percent: | | | | | | | | |
| Paraffin | 56.8 | 50.6 | 45.9 | 57.7 | 56.6 | 59.0 | 44.7 | 71.4 |
| Olefin | 7.4 | 1.2 | 2.1 | 9.7 | 9.8 | 10.1 | 4.9 | 0 |
| Aromatic | 35.8 | 48.2 | 52.0 | 32.6 | 33.7 | 31.0 | 50.4 | 28.6 |
| Monoalkylbenzenes | 11.1 | 33.8 | 28.5 | 12.6 | 30.3 | 2.4 | 24.6 | 12.0 |
| Polyalkylbenzenes | 19.8 | 14.2 | 23.0 | 12.8 | 3.1 | 28.3 | 25.6 | 9.7 |
| n-Paraffins | 19.8 | 14.8 | 11.4 | 20.0 | 19.3 | 20.2 | 23.1 | 17.7 |
| Isoparaffins | 35.0 | 35.3 | 34.0 | 34.7 | 34.2 | 35.7 | 18.9 | 52.6 |
| Cycloparaffins | 1.9 | .5 | .5 | 3.0 | 3.0 | 3.1 | 2.7 | 1.2 |

1/ Estimates of RON from fuel specified.

TABLE 1. - Experimental fuels used in the gasoline fuel test program (Cont'd)

| Specifications | Fuel No. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 |
| Grade | Special | Special | Special | Special | Special | Premium | Regular | Premium | Regular |
| RVP | 8.7 | 7.7 | 8.1 | 14.0 | 8.2 | 10.0 | 9.9 | 11.0 | 10.1 |
| Specific gravity | .748 | .745 | .751 | .723 | .761 | .728 | .738 | .769 | .744 |
| TEL, ml/gal | 0 | 0 | 0 | 0 | 0 | 2.6 | 2.0 | 0 | 0 |
| Research octane No. | 89 | 96 | 90 | 91 | 93 | 100 | 95 | 102 | 98 |
| Distillation, °F: | | | | | | | | | |
| IBP | 105 | 103 | 100 | 90 | 107 | 88 | 90 | 87 | 88 |
| 10 percent | 135 | 140 | 136 | 112 | 138 | 117 | 120 | 117 | 115 |
| 50 percent | 213 | 200 | 188 | 186 | 222 | 221 | 212 | 238 | 204 |
| 90 percent | 324 | 267 | 288 | 294 | 291 | 308 | 332 | 315 | 313 |
| End | 392 | 294 | 370 | 382 | 376 | 381 | 377 | 370 | 369 |
| GLC composition, mole percent: | | | | | | | | | |
| Paraffin | 43.5 | 51.5 | 62.1 | 59.0 | 43.2 | 61.4 | 62.3 | 39.9 | 48.5 |
| Olefin | 19.3 | 0 | 8.7 | 9.2 | 9.2 | 11.1 | 15.9 | 10.7 | 17.2 |
| Aromatic | 37.2 | 48.5 | 29.2 | 31.8 | 47.7 | 27.6 | 21.9 | 50.0 | 34.3 |
| Monoalkylbenzenes | 13.6 | 23.4 | 12.5 | 12.6 | 13.8 | 20.3 | 6.6 | 19.6 | 10.1 |
| Polyalkylbenzenes | 16.2 | 18.7 | 11.9 | 12.8 | 27.0 | 7.0 | 14.9 | 27.8 | 2[illegible]0 |
| n-Paraffins | 21.6 | 22.3 | 20.0 | 31.8 | 24.2 | 23.1 | 13.1 | 2.3 | 5.[illegible] |
| Isoparaffins | 17.6 | 26.3 | 10.3 | 24.2 | 15.4 | 37.3 | 39.9 | 36.1 | 40.2 |
| Cycloparaffins | 4.2 | 2.9 | 31.9 | 3.1 | 3.6 | 1.0 | 9.3 | .9 | 2.6 |

TABLE 2. - Experimental fuels used in the simple hydrocarbon fuel testing program

| |
|---|
| n-Butane |
| 2,2,4-Trimethylpentane |
| 2,3,4-Trimethylpentane |
| Methylcyclopentane |
| Butene-1 |
| cis and trans Hexenes - 2 and 3 |
| 2,4,4-Trimethylpentene-1 |
| 2,4,4-Trimethylpentene-2 |
| Benzene |
| Toluene |
| m-Xylene |
| sec-Butylbenzene |
| Hexene-1 + benzene |
| n-Heptane + benzene |
| n-Heptane + toluene |
| n-Heptane + m-xylene |
| n-Heptane + 2,4,4-trimethylpentene-2 |

TABLE 3. - Test automobiles

| Vehicle No. | Make | Model | Year | Engine displacement, CID | Compression ratio |
|---|---|---|---|---|---|
| 1 | Chevrolet | Impala | 1968 | 327 | 8.8 |
| 2 | Pontiac | Catalina | 1968 | 400 | 8.6 |
| 3 | Rambler | Ambassador | 1969 | 290 | 9.0 |
| 4 | Oldsmobile | Cutlass | 1969 | 350 | 10.3 |
| 5 | Chevrolet | Impala | 1970 | 350 | 9.0 |
| 6 | Plymouth | Fury | 1970 | 318 | 8.8 |
| 7 | Ford | Fairlane | 1970 | 351 | 9.5 |
| 8 | Chevrolet | Biscayne | 1971 | 350 | 8.5 |
| 9 | Ford | Custom | 1971 | 351 | 9.0 |
| 10 | Plymouth | Fury I | 1971 | 383 | 8.7 |
| 11 | Plymouth | Valiant | 1969 | 225 | 8.4 |

NOTE: Vehicles 1 through 4 were equipped to meet the California emission standards of 1968-1969.
Vehicles 5 through 10 were equipped with evaporative control devices.

TABLE 4. - Mass emissions and molar specific reactivity of exhaust in first phase of fleet testing program

(Each value is average of three tests)

| Vehicle No. | Fuel No. 1 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | Mean | Std. dev. 1/ | Coeff. var. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **HYDROCARBON, g/mile** | | | | | | | | | | | |
| 1 | 4.02 | 4.16 | 4.15 | 4.05 | 4.04 | 3.98 | 3.86 | 3.84 | 4.02 | 0.20 | 5.0 |
| 2 | 3.91 | 3.71 | 4.09 | 3.89 | 3.90 | 3.51 | 3.36 | 3.96 | 3.79 | .17 | 4.6 |
| 3 | 3.77 | 3.96 | 3.68 | 3.61 | 3.76 | 3.81 | 3.73 | 4.14 | 3.81 | .19 | 5.1 |
| 4 | 2.84 | 2.88 | 3.03 | 2.99 | 2.91 | 3.38 | 3.04 | 3.24 | 3.04 | .22 | 7.1 |
| 5 | 2.53 | 2.55 | 2.38 | 2.41 | 2.40 | 2.59 | 2.54 | 2.42 | 2.48 | .29 | 11.6 |
| 6 | 5.70 | 4.48 | 4.82 | 4.57 | 5.12 | 5.23 | 5.22 | 8.09 | 5.40 | .36 | 6.7 |
| 7 | 3.52 | 3.20 | 3.42 | 3.61 | 3.43 | 3.29 | 3.46 | 3.54 | 3.43 | .17 | 4.9 |
| 8 | 2.51 | 2.36 | 2.62 | 2.21 | 2.46 | 2.40 | 2.10 | 3.17 | 2.48 | .20 | 7.9 |
| 9 | 3.13 | 3.43 | 3.85 | 3.83 | 3.58 | 3.94 | 3.37 | 3.81 | 3.62 | .20 | 5.5 |
| Mean | 3.55 | 3.41 | 3.56 | 3.45 | 3.51 | 3.57 | 3.41 | 4.02 | | | |
| Std.dev.1/ | .26 | .23 | .24 | .19 | .21 | .21 | .26 | .29 | | | |
| Coeff. var. | 7.3 | 6.7 | 6.7 | 5.5 | 6.0 | 5.9 | 7.6 | 7.2 | | | |
| **CARBON MONOXIDE, g/mile** | | | | | | | | | | | |
| 1 | 37 | 34 | 32 | 32 | 29 | 26 | 25 | 30 | 30.8 | 4.0 | 13.0 |
| 2 | 38 | 32 | 34 | 32 | 29 | 27 | 21 | 34 | 30.7 | 2.8 | 9.2 |
| 3 | 40 | 39 | 35 | 36 | 34 | 40 | 34 | 42 | 37.6 | 4.4 | 11.6 |
| 4 | 48 | 47 | 44 | 54 | 53 | 56 | 43 | 57 | 50.2 | 4.7 | 9.3 |
| 5 | 42 | 35 | 28 | 32 | 38 | 48 | 45 | 36 | 38.0 | 8.0 | 21.0 |
| 6 | 71 | 55 | 54 | 48 | 59 | 70 | 62 | 106 | 65.7 | 5.3 | 8.0 |
| 7 | 34 | 29 | 32 | 33 | 34 | 34 | 33 | 38 | 33.2 | 3.2 | 9.8 |
| 8 | 30 | 28 | 26 | 24 | 34 | 35 | 28 | 53 | 32.4 | 3.6 | 11.2 |
| 9 | 30 | 35 | 34 | 33 | 37 | 49 | 34 | 47 | 37.4 | 3.8 | 10.3 |
| Mean | 41.2 | 37.0 | 35.5 | 36.2 | 38.5 | 42.8 | 36.2 | 49.7 | | | |
| Std.dev.1/ | 4.3 | 3.0 | 4.5 | 4.0 | 4.2 | 6.3 | 6.5 | 5.0 | | | |
| Coeff. var. | 10.4 | 8.1 | 12.6 | 11.0 | 10.8 | 14.6 | 17.8 | 10.0 | | | |

1/ Standard deviation calculated from the chree replicates on each car fuel combination.

TABLE 4. - Mass emissions and molar specific reactivity of exhaust in first phase of fleet testing program (cont'd)

(Each value is average of three tests)

| Vehicle No. | Fuel No. 1 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | Mean | Std. dev. 1/ | Coeff. var. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| NITRIC OXIDE, as $NO_2$, g/mile | | | | | | | | | | | |
| 1 | 6.7 | 8.2 | 6.7 | 7.3 | 7.9 | 6.5 | 8.4 | 7.4 | 7.4 | 0.7 | 9.8 |
| 2 | 10.0 | 10.8 | 11.5 | 10.1 | 13.0 | 8.6 | 9.8 | 11.4 | 10.7 | 1.1 | 10.1 |
| 3 | 5.6 | 5.8 | 5.9 | 6.2 | 7.1 | 5.5 | 6.5 | 5.8 | 6.1 | .5 | 7.9 |
| 4 | 5.0 | 5.7 | 5.4 | 5.9 | 4.6 | 4.3 | 5.5 | 5.6 | 5.1 | .3 | 5.1 |
| 5 | 2.6 | 3.0 | 2.7 | 2.6 | 2.2 | 2.6 | 2.5 | 2.6 | 2.6 | .2 | 8.9 |
| 6 | 5.1 | 5.5 | 5.6 | 5.8 | 5.0 | 5.5 | 5.2 | 4.5 | 5.3 | .3 | 5.4 |
| 7 | 3.7 | 3.7 | 3.6 | 3.3 | 3.1 | 3.9 | 3.4 | 3.6 | 3.5 | .3 | 7.9 |
| 8 | 3.6 | 3.5 | 3.4 | 3.3 | 3.3 | 3.7 | 3.5 | 3.7 | 3.5 | .2 | 6.1 |
| 9 | 4.1 | 4.9 | 5.3 | 5.2 | 4.0 | 4.9 | 4.6 | 4.5 | 4.7 | .5 | 10.7 |
| Mean | 5.2 | 5.7 | 5.6 | 5.3 | 5.6 | 5.1 | 5.5 | 5.5 | | | |
| Std.dev.1/ | .5 | .5 | .5 | .6 | .7 | .7 | .5 | .4 | | | |
| Coeff. var. | 9.1 | 8.5 | 9.3 | 11.0 | 11.8 | 13.0 | 9.0 | 7.3 | | | |
| TOTAL ALDEHYDES, g/mile | | | | | | | | | | | |
| 1 | 0.18 | 0.18 | 0.16 | 0.14 | 0.18 | 0.21 | 0.18 | 0.15 | 0.17 | 0.02 | 8.9 |
| 2 | .22 | .22 | .22 | .21 | .25 | .27 | .22 | .20 | .23 | .02 | 7.0 |
| 3 | .16 | .15 | .15 | .15 | .15 | .22 | .14 | .14 | .16 | .02 | 10.3 |
| 4 | .15 | .16 | .15 | .14 | .16 | .19 | .16 | .15 | .16 | .01 | 7.9 |
| 5 | .11 | .12 | .14 | .12 | .13 | .10 | .12 | .11 | .12 | .01 | 12.4 |
| 6 | .19 | .18 | .16 | .18 | .20 | .15 | .19 | .15 | .17 | .02 | 10.4 |
| 7 | .18 | .20 | .16 | .20 | .23 | .16 | .19 | .18 | .19 | .02 | 11.8 |
| 8 | .19 | .16 | .17 | .14 | .20 | .14 | .18 | .13 | .16 | .02 | 10.6 |
| 9 | .21 | .24 | .25 | .25 | .22 | .18 | .21 | .16 | .21 | .03 | 16.1 |
| Mean | .18 | .18 | .17 | .17 | .20 | .18 | .18 | .15 | | | |
| Std.dev.1/ | .01 | .02 | .03 | .02 | .03 | .02 | .02 | .02 | | | |
| Coeff. var. | 5.6 | 11.1 | 17.6 | 11.8 | 15.0 | 11.1 | 11.1 | 13.3 | | | |

1/ Standard deviation calculated from the three replicates on each car fuel combination.

TABLE 4. - Mass emissions and molar specific reactivity of exhaust in first phase of fleet testing program (cont'd)

(Each value is average of three tests)

| Vehicle No. | Fuel No. 1 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | Mean | Std. dev. 1/ | Coeff. var. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | EXHAUST HYDROCARBON REACTIVITIES, ETHYLENE EQUIVALENT, g/mile | | | | | | | | | | |
| 1 | 2.16 | 2.30 | 2.31 | 2.11 | 2.17 | 1.80 | 2.05 | 1.65 | 2.09 | 0.09 | 4.1 |
| 2 | 2.17 | 2.12 | 2.38 | 2.09 | 1.98 | 1.63 | 2.03 | 1.77 | 2.02 | .09 | 4.7 |
| 3 | 2.02 | 2.13 | 2.06 | 1.85 | 2.03 | 1.81 | 1.91 | 1.74 | 1.94 | .09 | 4.7 |
| 4 | 1.59 | 1.65 | 1.72 | 1.54 | 1.77 | 1.40 | 1.40 | 1.42 | 1.56 | .10 | 6.6 |
| 5 | 1.39 | 1.41 | 1.37 | 1.30 | 1.29 | 1.18 | 1.31 | 1.08 | 1.29 | .14 | 10.7 |
| 6 | 2.94 | 2.47 | 2.73 | 2.41 | 2.58 | 2.42 | 2.51 | 3.17 | 2.65 | .11 | 4.1 |
| 7 | 1.94 | 1.83 | 2.03 | 1.99 | 1.84 | 1.62 | 1.75 | 1.60 | 1.83 | .08 | 4.5 |
| 8 | 1.44 | 1.46 | 1.57 | 1.25 | 1.46 | 1.16 | 1.09 | 1.47 | 1.36 | .11 | 8.3 |
| 9 | 1.81 | 1.91 | 2.28 | 2.13 | 2.02 | 1.90 | 1.79 | 1.72 | 1.95 | .12 | 6.0 |
| Mean | 1.76 | 1.93 | 2.05 | 1.84 | 1.90 | 1.66 | 1.76 | 1.73 | | | |
| Std.dev. 1/ | .09 | .13 | .12 | .10 | .10 | .09 | .13 | .09 | | | |
| Coeff. var. | 4.3 | 6.2 | 5.8 | 5.4 | 5.1 | 5.4 | 7.6 | 5.1 | | | |

1/ Standard deviation calculated from the three replicates on each car fuel combination.

TABLE 5. - Mass emissions and molar specific reactivity of exhaust in second phase of fleet testing program

[Each value is an average of three tests, time weighted, according to the cold start transient and stabilized portions of the Federal test procedure for 1975 automobiles.]

| Vehicle No. | Fuel No. 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | Mean | Std. dev.[1] | Coeff. var. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EXHAUST HYDROCARBON, g/mile | | | | | | | | | | | | |
| 5 | 3.56 | 3.48 | 3.84 | 3.74 | 3.72 | 3.54 | 3.66 | 3.61 | 3.45 | 3.48 | 3.61 | 0.21 | 5.7 |
| 6 | 4.41 | 5.10 | 4.74 | 4.86 | 5.02 | 4.10 | 4.89 | 4.61 | 4.18 | 4.22 | 4.61 | .30 | 6.6 |
| 7 | 3.07 | 3.26 | 3.07 | 3.37 | 3.75 | 2.83 | 3.54 | 3.03 | 2.97 | 3.24 | 3.21 | .20 | 6.1 |
| 9 | 2.87 | 2.67 | 2.88 | 3.00 | 3.12 | 2.78 | 3.08 | 2.72 | 2.73 | 2.96 | 2.88 | .17 | 5.9 |
| 10 | 3.16 | 3.30 | 3.28 | 3.20 | 3.37 | 2.88 | 3.43 | 2.99 | 3.08 | 3.00 | 3.17 | .18 | 5.6 |
| Mean | 3.41 | 3.55 | 3.56 | 3.63 | 3.80 | 3.23 | 3.72 | 3.39 | 3.28 | 3.38 | | | |
| Std. dev.[1] | .29 | .29 | .33 | .21 | .14 | .20 | .23 | .13 | .18 | .07 | | | |
| Coeff. var. | 8.4 | 8.0 | 9.3 | 5.9 | 3.7 | 6.1 | 6.2 | 3.8 | 5.4 | 2.0 | | | |
| | EXHAUST CARBON MONOXIDE, g/mile | | | | | | | | | | | | |
| 5 | 71 | 71 | 72 | 70 | 66 | 65 | 65 | 74 | 62 | 62 | 67.9 | 5 1 | 7.5 |
| 6 | 43 | 46 | 46 | 46 | 44 | 44 | 46 | 48. | 44 | 45. | 45.3 | 2 4 | 5.2 |
| 7 | 40 | 43 | 40 | 44 | 44 | 38 | 43 | 44 | 40. | 44 | 42.0 | 2.9 | 6.9 |
| 9 | 39 | 35 | 38 | 36 | 41 | 36 | 42 | 40 | 40 | 40 | 38.7 | 3.4 | 8.8 |
| 10 | 42 | 45 | 42 | 41 | 42 | 39 | 46 | 44 | 47 | 42 | 43.1 | 2.9 | 6.8 |
| Mean | 47.1 | 48.2 | 47.4 | 48.5 | 48.8 | 44.4 | 48.4 | | | | | | |
| Std. dev.[1] | 3.4 | | 4.2 | 3.4 | 2.0 | 3.5 | | | 4.4 | 1.2 | | | |
| Coeff. var. | 7.3 | 10.2 | 8.9 | 7.2 | 4.1 | 7.8 | 7.3 | 6.5 | 9.4 | 2.7 | | | |
| | EXHAUST NITRIC OXIDE, as $NO_2$, g/mile | | | | | | | | | | | | |
| 5 | 4.5 | 4.1 | 4.2 | 4.9 | 4.1 | 5.0 | 4.8 | 4.6 | 4.6 | 4.9 | 4.6 | .3 | 5.7 |
| 6 | 6.9 | 6.8 | 6.5 | 7.2 | 6.8 | 7.3 | 7.0 | 7.2 | 6.8 | 7.2 | 7.0 | .1 | 1.7 |
| 7 | 5.0 | 4.7 | 4.7 | 5.6 | 5.0 | 5.3 | 5.5 | 5.1 | 5.3 | 5.6 | 5.2 | .3 | 5.4 |
| 9 | 6.1 | 6.1 | 6.1 | 6.7 | 5.8 | 6.9 | 6.2 | 6.1 | 6.0 | 6.6 | 6.3 | .3 | 4.8 |
| 10 | 6.1 | 5.8 | 5.7 | 6.5 | 5.5 | 6.7 | 6.1 | 6.3 | 5.7 | 6.6 | 6.1 | .2 | 3.4 |
| Mean | 5.7 | 5.5 | 5.4 | 6.2 | 5.4 | 6.3 | 5.9 | 5.9 | 5.7 | 6.2 | | | |
| Std. dev.[1] | .2 | .3 | .1 | .3 | .2 | .3 | .3 | .3 | .1 | .3 | | | |
| Coeff. var. | 3.3 | 6.0 | 2.6 | 4.0 | 4.3 | 4.1 | 5.5 | 4.5 | 1.6 | 4.7 | | | |

[1] Standard deviation calculated from the three replicates on each car fuel combination.

TABLE 5. - Mass emissions and molar specific reactivity of exhaust in second phase of fleet testing program (Continued)

[Each value is an average of three tests, time weighted, according to the cold start transient and stabilized portions of the Federal test procedure for 1975 automobiles.]

| Vehicle No. | Fuel No. 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | Mean | Std. 1/ dev. | Coeff. var. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| EXHAUST TOTAL ALDEHYDES, g/mile | | | | | | | | | | | | | |
| 5 | 0.11 | 0.11 | 0.10 | 0.10 | 0.13 | 0.12 | 0.13 | 0.11 | 0.13 | 0.09 | 0.11 | 0.01 | 13.3 |
| 6 | .18 | .17 | .19 | .16 | .17 | .17 | .16 | .17 | .17 | .15 | .17 | .02 | 8.9 |
| 7 | .16 | .14 | .14 | .15 | .19 | .14 | .15 | .13 | .15 | .15 | .15 | .01 | 8.9 |
| 9 | .18 | .18 | .17 | .17 | .19 | .17 | .16 | .16 | .17 | .15 | .17 | .01 | 8.7 |
| 10 | .16 | .15 | .17 | .14 | .17 | .16 | .14 | .14 | .15 | .14 | .15 | .01 | 9.8 |
| Mean | .16 | .15 | .15 | .14 | .17 | .15 | .15 | .14 | .15 | .14 | .15 | | |
| Std. dev. 1/ | .01 | .02 | .01 | .01 | .02 | .02 | .02 | .01 | .02 | .01 | | | |
| Coeff. var. | 8.7 | 10.1 | 9.4 | 9.1 | 9.4 | 10.0 | 11.0 | 9.2 | 11.7 | 9.5 | | | |
| JACKSON MOLAR SPECIFIC REACTIVITY, ethylene equivalents 2/ | | | | | | | | | | | | | |
| 5 | 0.87 | 0.86 | 0.97 | 0.86 | 0.87 | 0.95 | 0.83 | 0.87 | 0.90 | 0.91 | 0.89 | 0.03 | 3.5 |
| 6 | .96 | .92 | 1.03 | .90 | .93 | 1.00 | .83 | .91 | .95 | .96 | .94 | .03 | 2.7 |
| 7 | .95 | .89 | 1.03 | .86 | .85 | .99 | .85 | .91 | .91 | .90 | .91 | .03 | 3.7 |
| 9 | 1.02 | 1.04 | 1.11 | 1.00 | .94 | 1.06 | .90 | .94 | 1.02 | .96 | 1.00 | .03 | 3.0 |
| 10 | .95 | .92 | 1.05 | .94 | .93 | 1.00 | .86 | .93 | .91 | .97 | .95 | .03 | 3.5 |
| Mean | .95 | .92 | 1.04 | .92 | .90 | 1.00 | .86 | .91 | .94 | .94 | | | |
| Std. dev. 1/ | .04 | .02 | .02 | .02 | .03 | .03 | .04 | .04 | .02 | .02 | | | |
| Coeff. var. | 4.2 | 2.6 | 2.3 | 2.6 | 3.2 | 3.4 | 4.6 | 4.2 | 2.1 | 2.6 | | | |

1/ Standard deviation calculated from the three replicates on each car fuel combination.
2/ Molar reactivity of ethylene = 1.

TABLE 6. - Correlation of exhaust composition with fuel composition for car No. 5

| Exhaust composition parameter (Y) | Mean ($\bar{Y}$) | Standard deviation ($S_Y$) | $R_{SQ}$ 1/ | | | |
|---|---|---|---|---|---|---|
| | | | Model I 2/ | Model II 2/ | Model III 2/ | Model IV 2/ |
| Ethylene | 0.187 | 0.032 | 0.50 | 0.52 | 0.52 | 0.53 |
| Propylene | .0728 | .0116 | .68 | .69 | .69 | .69 |
| iso + 1-Butenes | .0177 | .0076 | .46 | .46 | .47 | .47 |
| 2-Methyl-2-butene | .0047 | .0019 | .002 | .073 | .007 | .008 |
| Toluene | .0596 | .0359 | .66 | .94 | .66 | .95 |
| m + p-Xylenes | .0324 | .0194 | .41 | .80 | .48 | .84 |
| $R_{Jackson}$ | .8610 | .0554 | .44 | .57 | .45 | .57 |
| $R_{EPA}$ | 2.467 | .122 | .12 | .55 | .15 | .55 |
| Formaldehyde | .0347 | .0099 | .11 | .17 | .19 | .21 |
| Total aldehydes | .0595 | .0147 | .13 | .16 | .15 | .17 |
| Total ppm hydrocarbon | 88.8 | 15.5 | .02 | .09 | .07 | .11 |
| Total reactive grams (ethylene equivalents) | 11.61 | 2.25 | .15 | .18 | .21 | .21 |

1/ $R_{SQ}$ = The square of the multiple correlation coefficient.

2/ Model I: $Y = a_1$ (mole fraction [MF] paraffins) + $a_2$ (MF olefins) + $a_3$ (MF aromatics)

Model II: $Y = a_1$ (paraffins) + $a_2$ (olefins) + $a_3$ (benzene) + $a_4$ (monoalkylbenzenes) + $a_5$ (polyalkylbenzenes)

Model III: $Y = a_1$ (n-paraffins) + $a_2$ (isoparaffins) + $a_3$ (olefins) + $a_4$ (aromatics)

Model IV: $Y = a_1$ (n-paraffins) + $a_2$ (isoparaffins) + $a_3$ (olefins) + $a_4$ (benzene) + $a_5$ (monoalkylbenzenes) + $a_6$ (polyalkylbenzenes)

TABLE 7. - Correlation of exhaust composition with fuel composition, car dummy variables, and air-fuel ratio

[Data from second phase of fleet testing program]

| Exhaust composition parameter | $R_{SQ}$ [1/] | | |
|---|---|---|---|
| | Model I [2/] | Model II [2/] | Model III [2/] |
| Ethylene | 0.41 | 0.85 | 0.45 |
| Propylene | .28 | .59 | .40 |
| iso + 1-Butenes | .35 | .71 | .46 |
| 2-Methyl-2-butene | .19 | .33 | .31 |
| Toluene | .44 | .47 | .44 |
| m + p-Xylenes | .42 | .44 | .42 |
| $R_{Jackson}$ | .26 | .72 | .35 |
| $R_{EPA}$ | .16 | .71 | .24 |
| Formaldehyde | .04 | .73 | .39 |
| Total aldehydes | .007 | .50 | .30 |
| Total ppm hydrocarbon | .07 | .84 | .18 |
| Total reactive grams (ethylene equivalents) | .10 | .75 | .16 |

1/ The square of multiple correlation coefficient.

2/ Model I: $Y = a_1$ (paraffins) + $a_2$ (olefins) + $a_3$ (aromatics)
Model II: $Y = a_1$ (paraffins) + $a_2$ (olefins) + $a_3$ (aromatics) + $a_4$ ($car_6$) + $a_5$ ($car_7$) + $a_6$ ($car_9$) + $a_7$ ($car_{10}$)
Model III: $Y = a_1$ (paraffins) + $a_2$ (olefins) + $a_3$ (aromatics) + $a_4$ (A/F)

TABLE 8. - Smog chamber reactivities of exhaust from fuels 1-21

| Fuel No. | Initial chamber concentrations | | | Reactivity data | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Maximum, ppm | | | | Dosages, ppm x min | | | |
| | $HC_i$, ppmC | $NO_{2_i}$, ppm | $\frac{HC}{NO_x}$ | $R_{NO_2}$, ppb/min | $O_3$ 1/ | PAN | PPN | HCHO | $O_3$ 1/ | PAN | PPN | HCHO |
| | 6 ppmC:1 ppm $NO_x$ | | | | | | | | | | | |
| 1 | 6.02 | 0.102 | 6.05 | 13.01 | 0.92 | 0.094 | 0.017 | 0.76 | 134 | 14.25 | 2.60 | 202 |
| | 6.06 | .105 | 6.10 | 12.88 | .90 | .099 | .017 | .81 | 134 | 14.91 | 2.69 | 198 |
| | 5.88 | .111 | 5.54 | 14.28 | .97 | .129 | .024 | .78 | 163 | 20.73 | 3.63 | 211 |
| | 5.90 | .099 | 5.84 | 13.73 | .85 | .102 | .019 | .84 | 149 | 17.21 | 3.22 | 226 |
| 2 | 6.07 | .089 | 6.04 | 11.86 | 1.03 | .101 | .015 | .72 | 151 | 14.66 | 2.10 | 195 |
| | 6.06 | .107 | 6.05 | 14.85 | .96 | .117 | .021 | .88 | 166 | 19.62 | 3.53 | 195 |
| | 5.96 | .102 | 5.92 | 15.41 | .98 | .118 | .022 | .84 | 182 | 21.53 | 3.86 | 217 |
| | 5.87 | .106 | 5.77 | 15.04 | .83 | .113 | .020 | .74 | 143 | 19.81 | 3.34 | 202 |
| | 6.05 | .101 | 5.99 | 11.97 | .91 | .089 | .021 | .66 | 133 | 13.06 | 3.04 | 177 |
| | 6.07 | .107 | 5.97 | 12.49 | .98 | .086 | .019 | .68 | 147 | 13.23 | 3.07 | 178 |
| 3 | 6.08 | .103 | 5.86 | 11.66 | .98 | .073 | .013 | .64 | 136 | 10.63 | 1.93 | 166 |
| | 6.09 | .105 | 6.01 | 12.32 | 1.04 | .077 | .015 | .96 | 152 | 12.14 | 2.31 | 232 |
| | 5.92 | .103 | 5.84 | 13.45 | .94 | .114 | .020 | .73 | 156 | 18.93 | 3.46 | 183 |
| | 6.09 | .098 | 5.98 | 14.30 | .90 | .117 | .022 | .87 | 165 | 20.97 | 3.91 | 215 |
| 4 | 6.00 | .099 | 5.90 | 12.90 | 1.02 | .083 | .018 | .65 | 159 | 13.27 | 2.72 | 175 |
| | 6.27 | .109 | 6.30 | 13.27 | .94 | .122 | .025 | .72 | 139 | 18.10 | 3.80 | 187 |
| | 6.07 | .107 | 5.90 | 15.39 | .96 | .120 | .025 | .67 | 171 | 21.56 | 4.38 | 173 |
| | 6.20 | .110 | 5.96 | 14.93 | .87 | .121 | .026 | .75 | 160 | 21.32 | 4.51 | 199 |
| 5 | 6.06 | .105 | 6.10 | 13.12 | 1.08 | .116 | .021 | .76 | 194 | 19.41 | 3.49 | 209 |
| | 6.05 | .106 | 6.03 | 11.84 | .96 | .114 | .024 | .81 | 152 | 17.66 | 3.75 | 202 |
| | 6.11 | .095 | 6.05 | 13.25 | .97 | .102 | .023 | .90 | 153 | 15.87 | 3.43 | 206 |
| | 6.03 | .095 | 6.25 | 12.30 | .87 | .123 | .029 | .81 | 142 | 19.12 | 4.32 | 208 |
| | 6.04 | .097 | 5.93 | 11.81 | .90 | .097 | .022 | .66 | 134 | 14.19 | 3.35 | 168 |
| | 6.06 | .089 | 6.14 | 10.23 | .86 | .089 | .024 | .65 | 119 | 13.86 | 3.43 | 158 |
| | 6.01 | .092 | 5.87 | 11.01 | .89 | .074 | .017 | .62 | 127 | 10.61 | 3.39 | 154 |
| | 6.03 | .095 | 5.98 | 11.35 | .86 | .106 | .026 | .66 | 123 | 15.23 | 3.84 | 170 |
| | 6.04 | .108 | 5.94 | 11.92 | .86 | .091 | .027 | .74 | 127 | 13.17 | 3.97 | 201 |
| | 6.05 | .114 | 6.58 | 10.77 | .92 | .100 | .028 | .72 | 146 | 15.42 | 4.20 | 196 |
| | 6.06 | .103 | 6.04 | 11.51 | .88 | .087 | .025 | .67 | 126 | 12.57 | 3.56 | 178 |

1/ Measured with the chemiluminescence ozone detector.

TABLE 8. - Smog chamber reactivities of exhaust from fuels 1-21 (Cont'd)

| Fuel No. | Initial chamber concentrations | | | Reactivity data | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $HC_i$, ppmC | $NO_{2_i}$, ppm | $\frac{HC}{NO_x}$ | $R_{NO_2}$, ppb/min | Maximum, ppm | | | | Dosages, ppm x min | | | |
| | | | | | $O_3$ 1/ | PAN | PPN | HCHO | $O_3$ 1/ | PAN | PPN | HCHO |
| | 6 ppmC:1 ppm $NO_x$ (cont'd) | | | | | | | | | | | |
| 6 | 6.02 | 0.101 | 5.90 | 11.87 | 1.04 | 0.066 | 0.016 | 0.88 | 146 | 10.15 | 2.15 | 209 |
| | 6.04 | .101 | 5.86 | 11.58 | 1.01 | .081 | .014 | .79 | 140 | 12.74 | 2.13 | 194 |
| | 6.00 | .104 | 5.88 | 12.36 | .95 | .091 | .019 | .84 | 142 | 13.46 | 2.72 | 224 |
| | 6.15 | .102 | 6.18 | 12.38 | .84 | .101 | .021 | .84 | 132 | 15.38 | 3.13 | 210 |
| 7 | 6.04 | .088 | 6.00 | 11.09 | .73 | .058 | .013 | .68 | 96 | 7.23 | 1.66 | 188 |
| | 5.97 | .092 | 5.93 | 11.11 | .70 | .058 | .012 | .65 | 95 | 8.77 | 1.80 | 187 |
| | 6.01 | .094 | 6.18 | 11.04 | .81 | .082 | .018 | .66 | 113 | 10.94 | 2.30 | 182 |
| | 6.09 | .098 | 6.04 | 11.17 | .87 | .079 | .016 | .76 | 121 | 10.87 | 2.17 | 217 |
| 8 | 5.98 | .096 | 5.88 | 12.47 | .87 | .088 | .015 | .56 | 130 | 12.92 | 2.27 | 147 |
| | 5.99 | .091 | 5.94 | 10.96 | .89 | .091 | .016 | .61 | 137 | 14.99 | 2.58 | 157 |
| | 6.02 | .096 | 5.99 | 11.52 | .84 | .088 | .014 | .61 | 125 | 13.51 | 2.43 | 159 |
| | 6.04 | .100 | 5.83 | 11.54 | .88 | .098 | .018 | .58 | 136 | 15.20 | 2.64 | 153 |
| | 6.05 | .103 | 6.02 | 10.42 | .88 | .106 | .02 | .59 | 126 | 15.62 | 2.71 | 159 |
| 9 | 6.00 | .104 | 6.02 | 11.57 | .89 | .088 | .018 | .85 | 136 | 13.75 | 2.68 | 203 |
| | 6.00 | .101 | 5.93 | 11.94 | .88 | .092 | .017 | .69 | 128 | 13.50 | 2.44 | 174 |
| | 6.09 | .098 | 6.05 | 11.86 | .91 | .103 | .02 | .78 | 140 | 15.38 | 2.99 | 195 |
| | 6.06 | .096 | 6.13 | 10.26 | .84 | .083 | .016 | .66 | 113 | 11.89 | 2.21 | 176 |
| 10 | 5.99 | .089 | 6.07 | 10.37 | .78 | .060 | .009 | .63 | 103 | 9.29 | 1.44 | 153 |
| | 6.01 | .086 | 5.62 | 10.60 | .69 | .055 | .009 | .55 | 86 | 8.47 | 1.26 | 141 |
| | 5.96 | .100 | 6.03 | 9.44 | .72 | .072 | .010 | .58 | 93 | 9.56 | 1.29 | 141 |
| | 5.99 | .087 | 5.73 | 9.13 | .66 | .058 | .010 | .57 | 79 | 8.31 | 1.16 | 154 |
| 11 | 6.16 | .104 | 6.14 | 11.44 | .9[illegible] | .116 | .013 | .74 | 152 | 18.97 | 2.16 | 160 |
| | 6.03 | .106 | 5.88 | 12.70 | .96 | .120 | .014 | .66 | 163 | 20.26 | 2.18 | 157 |
| | 6.08 | .103 | 6.02 | 12.58 | .85 | .122 | .013 | .65 | 158 | 21.75 | 2.32 | 183 |
| 12 | 6.03 | .102 | 6.03 | 11.5 | .68 | .07 | .007 | .55 | 92 | 10.23 | .97 | 152 |
| | 5.93 | .101 | 5.94 | 11.8 | .74 | .07 | .007 | .59 | 102 | 9.77 | 1.05 | 164 |
| | 5.97 | .109 | 5.92 | 11.4 | .63 | .06 | .006 | .54 | 83 | 9.03 | .89 | 159 |

1/ Measured with the chemiluminescence ozone detector.

TABLE 8. - Smog chamber reactivities of exhaust from fuels 1-21 (Cont'd)

| Fuel No. | Initial chamber concentrations | | | Reactivity data | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Maximum, ppm | | | | Dosages, ppm x min | | | |
| | $HC_i$, ppmC | $NO_{2_i}$, ppm | $\frac{HC}{NO_x}$ | $R_{NO_2}$, ppb/min | $O_3$ 1/ | PAN | PPN | HCHO | $O_3$ 1/ | PAN | PPN | HCHO |
| 6 ppmC:1 ppm $NO_x$ (cont'd) | | | | | | | | | | | | |
| 13 | 6.01 | 0.091 | 6.40 | 10.3 | 0.60 | 0.05 | 0.006 | 0.64 | 72 | 6.44 | 0.76 | 191 |
| | 5.95 | .099 | 5.88 | 9.7 | .52 | .04 | .005 | .72 | 58 | 5.20 | .65 | 185 |
| 14 | 6.03 | .100 | 5.59 | 10.9 | .80 | .10 | .008 | .77 | 107 | 13.87 | 1.07 | 200 |
| | 5.97 | .103 | 5.83 | 12.5 | .93 | .11 | .008 | .67 | 135 | 15.56 | 1.18 | 182 |
| 15 | 6.05 | .099 | 5.81 | 11.2 | .81 | .10 | .006 | .71 | 111 | 13.66 | .86 | 185 |
| | 6.00 | .104 | 5.89 | 10.8 | .93 | .09 | .006 | .48 | 125 | 12.92 | .75 | 119 |
| 16 | 5.98 | .101 | 5.93 | 10.5 | .64 | .06 | .003 | .60 | 76 | 7.79 | .43 | 176 |
| | 6.00 | .104 | 5.95 | 10.3 | .63 | .05 | .003 | .58 | 73 | 6.32 | .34 | 154 |
| 17 | 6.05 | .105 | 5.92 | 11.5 | .68 | .08 | .013 | .62 | 90 | 10.58 | 1.61 | 169 |
| | 6.08 | .103 | 6.12 | 11.3 | .79 | .07 | .010 | .79 | 102 | 9.29 | 1.39 | 164 |
| 18 | 6.05 | .100 | 5.85 | 10.6 | .67 | .06 | .003 | .54 | 81 | 8.38 | .38 | 149 |
| | 6.05 | .105 | 5.92 | 9.5 | .66 | .05 | .003 | .45 | 77 | 6.83 | .33 | 117 |
| 19 | 6.00 | .103 | 6.00 | 10.3 | .61 | .05 | .006 | .60 | 75 | 6.59 | .75 | 160 |
| | 5.99 | .103 | 5.90 | 11.0 | .75 | .05 | .006 | .52 | 95 | 6.73 | .76 | 141 |
| 20 | 6.00 | .100 | 5.98 | 11.2 | .64 | .06 | .006 | .71 | 78 | 7.49 | .80 | 185 |
| | 6.01 | .103 | 5.93 | 10.5 | .70 | .05 | .006 | .56 | 87 | 7.43 | .80 | 159 |
| 21 | 6.07 | .097 | 5.80 | 10.2 | .69 | .08 | .007 | .75 | 84 | 10.57 | .98 | 167 |
| | 6.02 | .100 | 5.99 | 10.5 | .87 | .08 | .007 | .52 | 111 | 11.42 | .96 | 141 |

1/Measured with the chemiluminescence ozone detector.

TABLE 8. - Smog chamber reactivities of exhaust from fuels 1-21 (Cont'd)

| Fuel No. | Initial chamber concentrations | | | Reactivity data | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Maximum, ppm | | | | Dosages, ppm x min | | | |
| | $HC_i$, ppmC | $NO_{2_i}$, ppm | $\frac{HC}{NO_x}$ | $R_{NO_2}$, ppb/min | $O_3$ 1/ | PAN | PPN | HCHO | $O_3$ 1/ | PAN | PPN | HCHO |
| | 3 ppmC:1/2 ppm $NO_x$ | | | | | | | | | | | |
| 1 | 3.00 | 0.050 | 6.04 | 6.11 | 0.53 | 0.041 | 0.008 | 0.41 | 80 | 6.40 | 1.14 | 106 |
| | 3.02 | .053 | 6.01 | 6.13 | .68 | .049 | .009 | .38 | 105 | 7.97 | 1.39 | 106 |
| | 3.00 | .045 | 6.04 | 5.62 | .54 | .040 | .008 | .45 | 80 | 6.37 | 1.14 | 112 |
| | 2.96 | .048 | 6.08 | 6.60 | .63 | .050 | .010 | .40 | 104 | 8.23 | 1.50 | 112 |
| 2 | 3.07 | .048 | 6.38 | 5.62 | .53 | .040 | .008 | .33 | 80 | 6.65 | 1.17 | 89 |
| | 3.04 | .046 | 5.94 | 6.36 | .61 | .047 | .009 | .33 | 95 | 7.70 | 1.47 | 84 |
| | 3.03 | .048 | 6.46 | 5.95 | .63 | .051 | .011 | .47 | 101 | 8.69 | 1.72 | 113 |
| | 3.04 | .045 | 6.24 | 6.40 | .65 | .057 | .012 | .40 | 107 | 9.64 | 1.88 | 108 |
| 3 | 3.06 | .050 | 6.13 | 5.85 | .56 | .040 | .008 | .45 | 86 | 6.37 | 1.26 | 97 |
| | 3.02 | .049 | 6.03 | 6.98 | .68 | .051 | .010 | .41 | 115 | 8.76 | 1.62 | 119 |
| | 3.00 | .045 | 6.17 | 6.76 | .62 | .049 | .009 | .42 | 105 | 8.54 | 1.58 | 109 |
| | 3.03 | .044 | 6.19 | 6.11 | .60 | .049 | .009 | .40 | 96 | 7.88 | 1.36 | 109 |
| 4 | 3.04 | .046 | 6.16 | 6.50 | .64 | .046 | .011 | .43 | 106 | 8.15 | 1.73 | 100 |
| | 3.03 | .045 | 5.99 | 6.43 | .62 | .053 | .013 | .40 | 101 | 8.68 | 1.96 | 101 |
| | 3.02 | .049 | 6.02 | 7.00 | .62 | .051 | .011 | .41 | 107 | 8.85 | 1.91 | 108 |
| | 3.02 | .046 | 6.13 | 7.63 | .69 | .051 | .011 | .38 | 119 | 9.08 | 1.95 | 95 |
| 5 | 3.04 | .046 | 6.02 | 7.19 | .62 | .047 | .010 | .56 | 102 | 7.96 | 1.73 | 114 |
| | 3.04 | .050 | 6.23 | 6.46 | .61 | .046 | .011 | .33 | 97 | 7.29 | 1.66 | 80 |
| | 3.00 | .047 | 5.99 | 6.21 | .60 | .046 | .012 | .35 | 94 | 7.34 | 1.68 | 104 |
| | 3.01 | .048 | 6.29 | 6.48 | .68 | .051 | .013 | .38 | 114 | 8.68 | 1.96 | 108 |
| 6 | 2.93 | .045 | 6.08 | 6.00 | .63 | .045 | .010 | .42 | 98 | 7.15 | 1.58 | 117 |
| | 2.99 | .046 | 6.00 | 6.49 | .62 | .049 | .010 | .38 | 100 | 7.78 | 1.56 | 109 |
| | 3.02 | .047 | 5.97 | 6.04 | .61 | .043 | .009 | .37 | 92 | 6.30 | 1.34 | 105 |
| | 3.03 | .044 | 5.97 | 6.33 | .61 | .045 | .010 | .41 | 94 | 6.87 | 1.40 | 115 |
| 11 | 3.06 | .050 | 6.13 | 5.60 | .58 | .043 | .005 | .28 | 84 | 7.13 | .77 | 73 |
| | 2.98 | .048 | 5.91 | 6.51 | .66 | .050 | .006 | .34 | 110 | 9.09 | .93 | 95 |
| | 3.02 | .047 | 6.26 | 5.28 | .62 | .045 | .004 | .39 | 93 | 7.45 | .85 | 100 |
| | 3.00 | .042 | 6.15 | 6.35 | .63 | .053 | .006 | .40 | 109 | 9.83 | 1.02 | 105 |

1/ Measured with the chemiluminescence ozone detector.

TABLE 8. - Smog chamber reactivities of exhaust from fuels 1-21 (Cont'd)

| Fuel No. | Initial chamber concentrations | | | Reactivity data | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Maximum, ppm | | | | Dosages, ppm x min | | | |
| | $HC_i$, ppmC | $NO_{2_i}$, ppm | $\frac{HC}{NO_x}$ | $R_{NO_2}$, ppb/min | $O_3$ 1/ | PAN | PPN | HCHO | $O_3$ 1/ | PAN | PPN | HCHO |
| | 3 ppmC:1/2 ppm $NO_x$ | | | | | | | | | | | |
| 12 | 2.66 | 0.049 | 5.40 | 6.55 | 0.38 | 0.023 | 0.002 | 0.48 | 61 | 3.43 | 0.29 | 155 |
| | 3.01 | .052 | 5.96 | 6.19 | .47 | .031 | .003 | .37 | 70 | 4.65 | .44 | 103 |
| 13 | 3.04 | .054 | 5.73 | 6.38 | .42 | .025 | .003 | .35 | 58 | 4.20 | .36 | 97 |
| | 3.03 | .053 | 6.17 | 6.19 | .51 | .037 | .004 | .43 | 78 | 5.61 | .52 | 120 |
| 14 | 2.98 | .053 | 5.96 | 6.58 | .52 | .049 | .004 | .33 | 82 | 7.93 | .62 | 93 |
| | 3.01 | .055 | 6.02 | 5.56 | .54 | .040 | .004 | .45 | 84 | 6.16 | .56 | 122 |
| 15 | 3.01 | .055 | 5.89 | 6.71 | .56 | .048 | .003 | .35 | 87 | 7.80 | .44 | 100 |
| | 3.01 | .059 | 6.15 | 6.40 | .58 | .045 | .003 | .34 | 97 | 7.24 | .45 | 99 |
| 16 | 3.01 | .059 | 5.98 | 6.32 | .50 | .034 | .002 | .36 | 73 | 5.02 | .23 | 98 |
| | 3.00 | .051 | 5.93 | 6.15 | .48 | .032 | .002 | .33 | 71 | 4.68 | .21 | 109 |
| 17 | 3.01 | .051 | 5.93 | 6.97 | .53 | .038 | .006 | .45 | 78 | 6.02 | .81 | 127 |
| | 3.03 | .050 | 6.05 | 6.12 | .51 | .036 | .005 | .46 | 76 | 5.31 | .68 | 117 |
| 18 | 3.04 | .054 | 6.08 | 6.21 | .52 | .037 | .002 | .38 | 77 | 5.74 | .30 | 109 |
| | 3.03 | .049 | 5.98 | 6.04 | .54 | .040 | .002 | .39 | 80 | 5.95 | .29 | 104 |
| 19 | 3.01 | .051 | 6.04 | 6.94 | .55 | .031 | .004 | .47 | 83 | 4.76 | .51 | 130 |
| | 3.13 | .055 | 6.12 | 6.99 | .60 | .042 | .005 | .49 | 94 | 6.29 | .66 | 124 |
| 20 | 3.00 | .056 | 5.90 | 6.74 | .52 | .038 | .004 | .39 | 78 | 5.94 | .59 | 110 |
| | 3.07 | .061 | 6.18 | 6.33 | .53 | .038 | .004 | .43 | 79 | 5.48 | .54 | 112 |
| | 3.09 | .054 | 6.19 | 5.42 | .46 | .036 | .004 | .41 | 65 | 5.02 | .49 | 112 |
| 21 | 3.08 | .054 | 5.94 | 6.35 | .56 | .044 | .004 | .41 | 83 | 6.84 | .57 | 107 |
| | 3.06 | .048 | 6.04 | 6.52 | .56 | .053 | .005 | .37 | 88 | 8.03 | .68 | 103 |
| | 3.00 | .055 | 5.78 | 5.76 | .45 | .039 | .003 | .37 | 66 | 5.78 | .49 | 97 |

1/Measured with the chemiluminescence ozone detector.

TABLE 9. - Smog chamber reactivities of exhaust from fuels 22-25

| Fuel No. | Initial chamber concentrations | | | REACTIVITY DATA | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Maximum, ppm | | | | Dosages, ppm x min | | | |
| | $HC_i$, ppmC | $NO_{2_i}$, ppm | $\frac{HC}{NO_x}$ | $R_{NO_2}$, ppb/min | $O_3$ [1/] | PAN | PPN | HCHO | $O_3$ [1/] | PAN | PPN | HCHO |
| | 6 ppmC:1 ppm $NO_x$ | | | | | | | | | | | |
| 22 | 5.96 | 0.099 | 5.92 | 10.5 | 0.68 | 0.07 | 0.008 | 0.72 | 87 | 9.48 | 1.12 | 189 |
| | 6.05 | .104 | 6.06 | 10.8 | .62 | .06 | .008 | .67 | 72 | 8.26 | .98 | 177 |
| 23 | 6.01 | .103 | 5.97 | 12.4 | .80 | .09 | .012 | .75 | 122 | 13.71 | 1.74 | 192 |
| | 6.02 | .102 | 6.04 | 11.6 | .75 | .09 | .012 | .89 | 106 | 13.17 | 1.19 | 204 |
| 24 | 6.04 | .104 | 5.97 | 10.9 | .71 | .10 | .008 | .67 | 101 | 14.44 | 1.15 | 174 |
| | 6.04 | .109 | 5.95 | 10.7 | .77 | .12 | .010 | .62 | 115 | 18.28 | 1.54 | 166 |
| 25 | 6.05 | .100 | 6.13 | 12.7 | .71 | .08 | .011 | .68 | 102 | 12.44 | 1.58 | 190 |
| | 5.96 | .101 | 5.97 | 10.9 | .72 | .10 | .011 | .71 | 99 | 14.62 | 1.69 | 204 |

1/ Measured with the chemiluminescence ozone detector.

TABLE 10. - Bureau of Mines rate-of-$NO_2$-formation reactivity scale 1/

| Exhaust component or group | Bureau of Mines specific $R_{NO_2}$ reactivity in propylene equivalents |
|---|---|
| Ethylene | 0.47 |
| Propylene | 1.00 |
| 1-Alkenes | .65 |
| Int-Alkenes | 3.78 |
| Diolefins | 1.41 |
| $C_{4+}$ Paraffins 2/ | .18 |
| Benzene | .15 |
| R-benzyls 3/ | .49 |
| R-nonbenzyls 4/ | .45 |
| $R_x$-benzenes 5/ | 1.19 |
| Formaldehyde | .79 |
| Aliphatic aldehydes | 1.41 |
| o-Tolualdehyde | 5.98 |
| Aromatic aldehydes | .19 |

1/ Smog chamber experiments involving several typical exhaust aldehydes as reported in reference 5 and reported results involving 19 typical exhaust hydrocarbons.
2/ Excludes methane, ethane, and propane.
3/ Includes toluene, ethylbenzene, n-propylbenzene, etc.
4/ Includes iso-propylbenzene, t-butyl benzene, etc.
5/ Includes the xylenes, mesitylene, and other polysubstituted benzenes.

TABLE 11. - Composition and smog chamber reactivities of exhaust from simple hydrocarbon fuels

| Fuel | Concentrations in raw wet exhaust, ppm | | | Jackson reactivity, propylene equivalents | EPA[1/] reactivity, propylene equivalents | Chamber reactivity, propylene equivalents | |
|---|---|---|---|---|---|---|---|
| | Hydrocarbon | Formaldehyde | Total aldehydes | | | $R_{NO_2}$ | Maximum $O_3$ |
| n-Butane | 1,058 | 14.3 | 22.8 | 0.24 | 0.22 | 0.43 | 0.16 |
| | 1,369 | 15.2 | 21.8 | .23 | .22 | .42 | .18 |
| n-Heptane + benzene | 879 | 12.3 | 29.7 | .24 | .23 | .59 | .15 |
| | 925 | 12.3 | 36.8 | .26 | .23 | .58 | .16 |
| 2,4,4-Trimethylpentane | 960 | 8.1 | 22.1 | .32 | .30 | .53 | .36 |
| | 1,260 | 17.1 | 28.8 | .25 | .24 | .48 | .29 |
| 2,3,4-Trimethylpentane | 1,122 | 17.8 | 31.7 | .51 | .34 | .78 | .63 |
| | 1,177 | 14.4 | 27.7 | .46 | .31 | .76 | .61 |
| Methylcyclopentane | 913 | 8.8 | 24.2 | .47 | .27 | 1.00 | .37 |
| | 999 | 11.2 | 16.1 | .44 | .26 | .94 | .33 |
| Butene-1 | 1,085 | 20.4 | 39.3 | .48 | .51 | .66 | .66 |
| | 1,400 | 19.5 | 26.2 | .44 | .47 | .57 | .59 |
| Hexene-1 + benzene | 960 | 16.2 | 26.2 | .30 | .33 | .58 | .29 |
| | 1,099 | 12.1 | 19.5 | .28 | .31 | .54 | .33 |
| 2,4,4-Trimethylpentene-1 | 1,089 | 17.7 | 40.0 | .47 | .48 | .75 | .74 |
| | 1,371 | 20.5 | 41.0 | .46 | .47 | .83 | .73 |
| Mixed 2- and 3-hexenes | 1,134 | 23.4 | 51.6 | .58 | .47 | .94 | .66 |
| | 1,227 | 19.1 | 43.2 | .53 | .45 | .89 | .58 |
| 2,4,4-Trimethylpentene-2 | 1,090 | 14.0 | 36.7 | .61 | .40 | 1.86 | .75 |
| | 1,234 | 23.1 | 36.7 | .57 | .38 | 1.78 | .71 |
| Benzene | 723 | 8.5 | 14.3 | .13 | .06 | .67 | .03 |
| | 939 | 10.1 | 15.6 | .12 | .06 | .66 | .02 |
| Toluene | 703 | 7.3 | 17.2 | .30 | .31 | .87 | .36 |
| | 755 | 7.1 | 17.9 | .28 | .29 | .87 | .35 |
| | 857 | 4.5 | 14.9 | .27 | .29 | .84 | .31 |

1/ Calculated using the EPA reactivity scale normalized to propylene reactivity = 1.0.

TABLE 11 . - Composition and smog chamber reactivities of exhaust from simple hydrocarbon fuels (continued)

| Fuel | Concentrations in raw wet exhaust, ppm | | | Jackson reactivity, propylene equivalents | EPA 1/ reactivity, propylene equivalents | Chamber reactivity, propylene equivalents | |
|---|---|---|---|---|---|---|---|
| | Hydrocarbon | Formaldehyde | Total aldehydes | | | $R_{NO_2}$ | Maximum $O_3$ |
| sec-Butylbenzene . . | 736 | 12.3 | 28.9 | 0.35 | 0.29 | 0.84 | 0.23 |
| | 862 | 12.7 | 35.1 | .32 | .27 | .79 | .23 |
| m-Xylene . . . . . | 587 | 5.9 | 22.6 | .65 | .54 | 1.57 | 1.33 |
| | 806 | 3.7 | 11.6 | .64 | .53 | 1.55 | 1.39 |
| n-Heptane + toluene | 989 | 13.9 | 36.5 | .29 | .30 | .67 | .41 |
| n-Heptane + m-xylene | 987 | 8.1 | 22.8 | .42 | .38 | .97 | .92 |
| n-Heptane + 2,4,4-trimethylpentene-2 | 1,520 | 20.5 | 41.0 | .44 | .34 | 1.01 | .70 |

1/ Calculated using the EPA reactivity scale normalized to propylene reactivity = 1.0.

TABLE 12. - Summary of smog chamber reactivities of exhaust from simple fuels

| Fuel | Reactivity, propylene equivalents | |
|---|---|---|
| | $R_{NO_2}$ | Maximum $O_3$ |
| n-Butane | 0.4 | 0.2 |
| n-Heptane | 1/ .5 | 1/ .4 |
| 2,2,4-Trimethylpentane | .5 | .3 |
| 2,3,4-Trimethylpentane | .8 | .6 |
| Methylcyclopentane | 1.0 | .4 |
| Butene-1 | .6 | .6 |
| Hexene-1 | 1/ .5 | 1/ .6 |
| 2,4,4-Trimethylpentene-1 | .8 | .7 |
| Hexene-2,3 | .9 | .6 |
| 2,4,4-Trimethylpentene-2 | 1.8 | .7 |
| Benzene | .7 | 0 |
| Toluene | .9 | .3 |
| sec-Butylbenzene | .8 | .2 |
| m-Xylene | 1.6 | 1.3 |
| n-Heptane + toluene | .7 | .4 |
| n-Heptane + m-xylene | 1.0 | .9 |
| n-Heptane + 2,4,4-trimethylpentene-2 | 1.0 | .7 |

1/ Gross estimates obtained from comparison of data from the n-heptane mixtures with aromatics versus data from the aromatics alone.

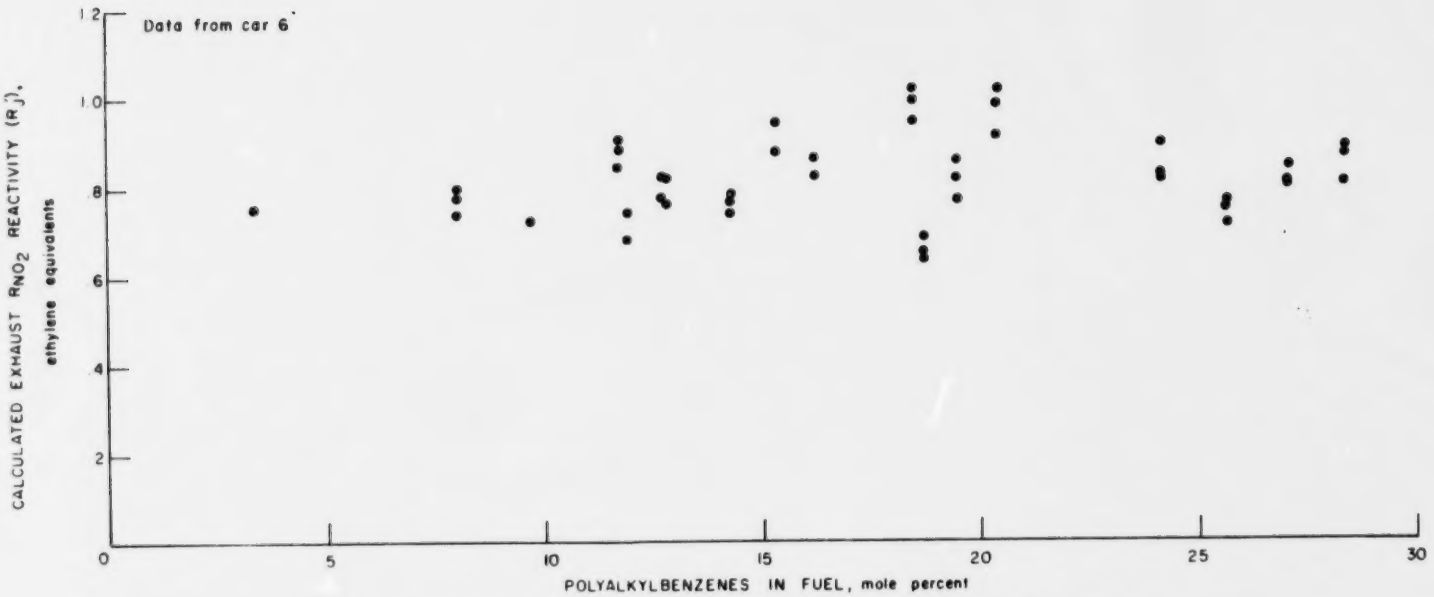


FIGURE 1.- Correlation of Calculated Exhaust Reactivities With Polyalkylbenzene Levels in Fuel.

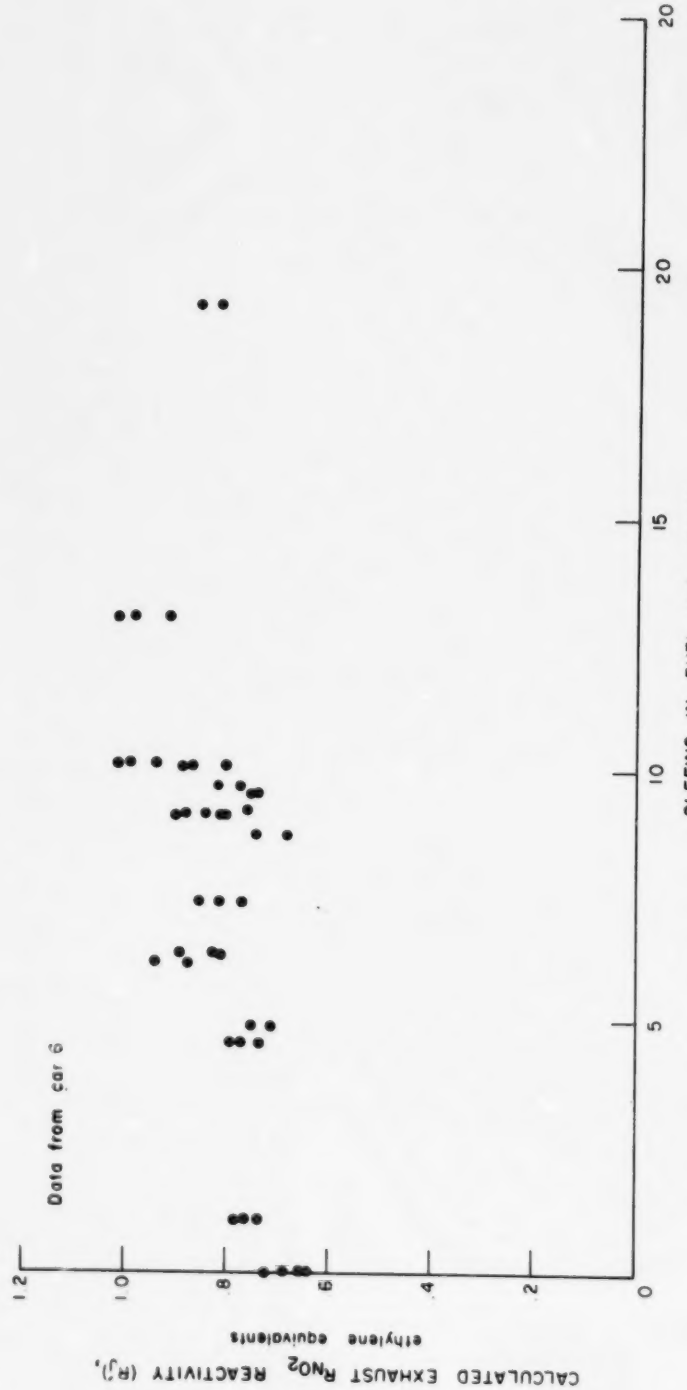


FIGURE 2.– Correlation of Calculated Exhaust Reactivities With Olefin Levels in Fuel.

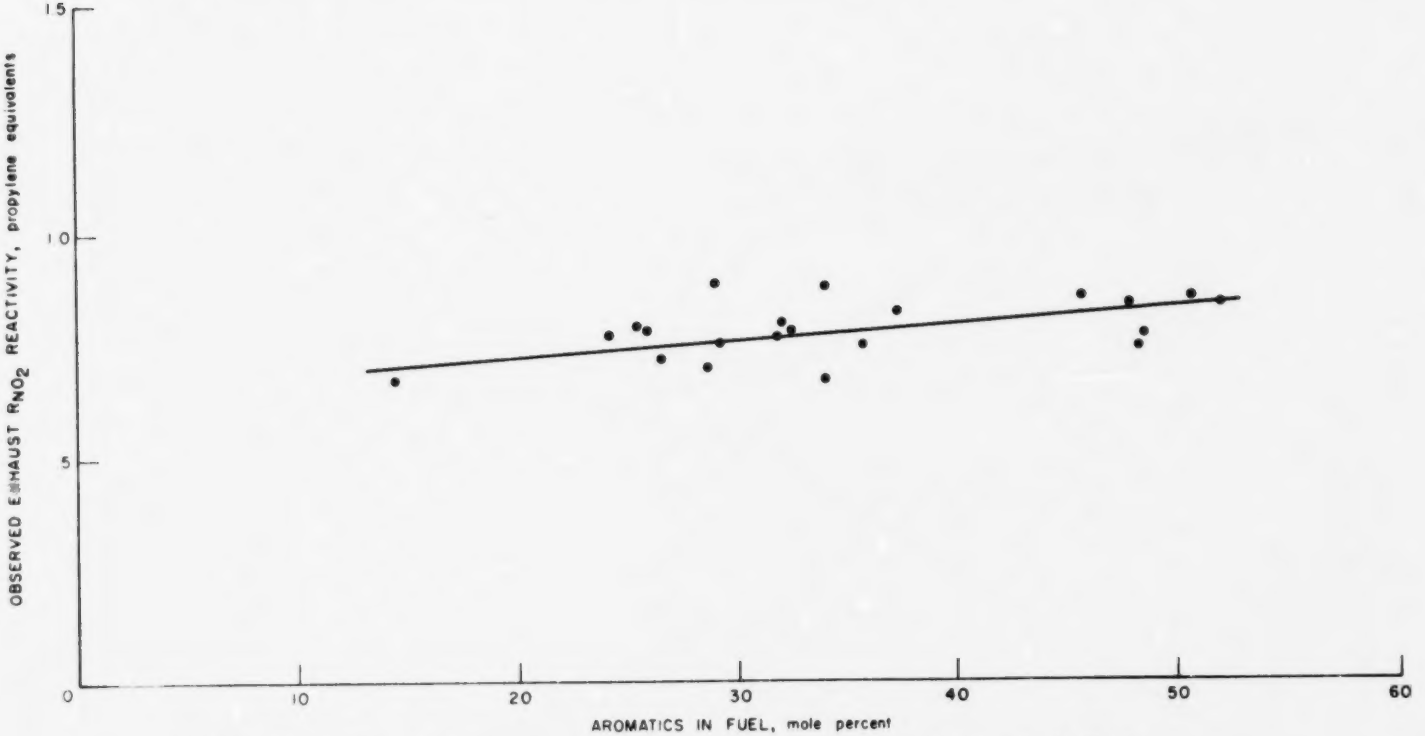


FIGURE 3.- Correlation of Observed Exhaust Reactivities With Total Aromatic Levels in Fuel.

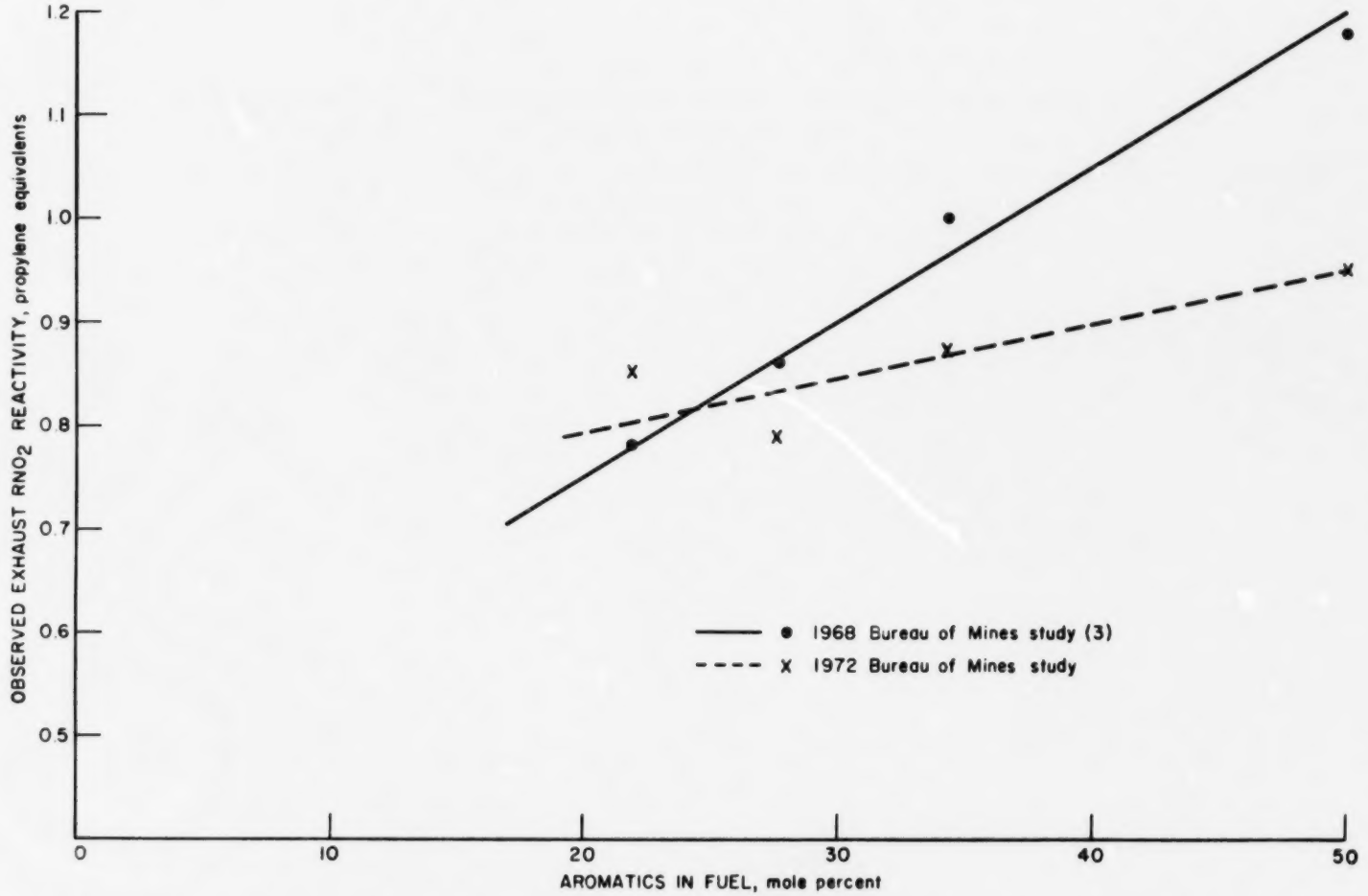


FIGURE 4 - Comparison of Exhaust Reactivities -- Fuel Aromatic Relationships From Two Bureau of Mines Studies.

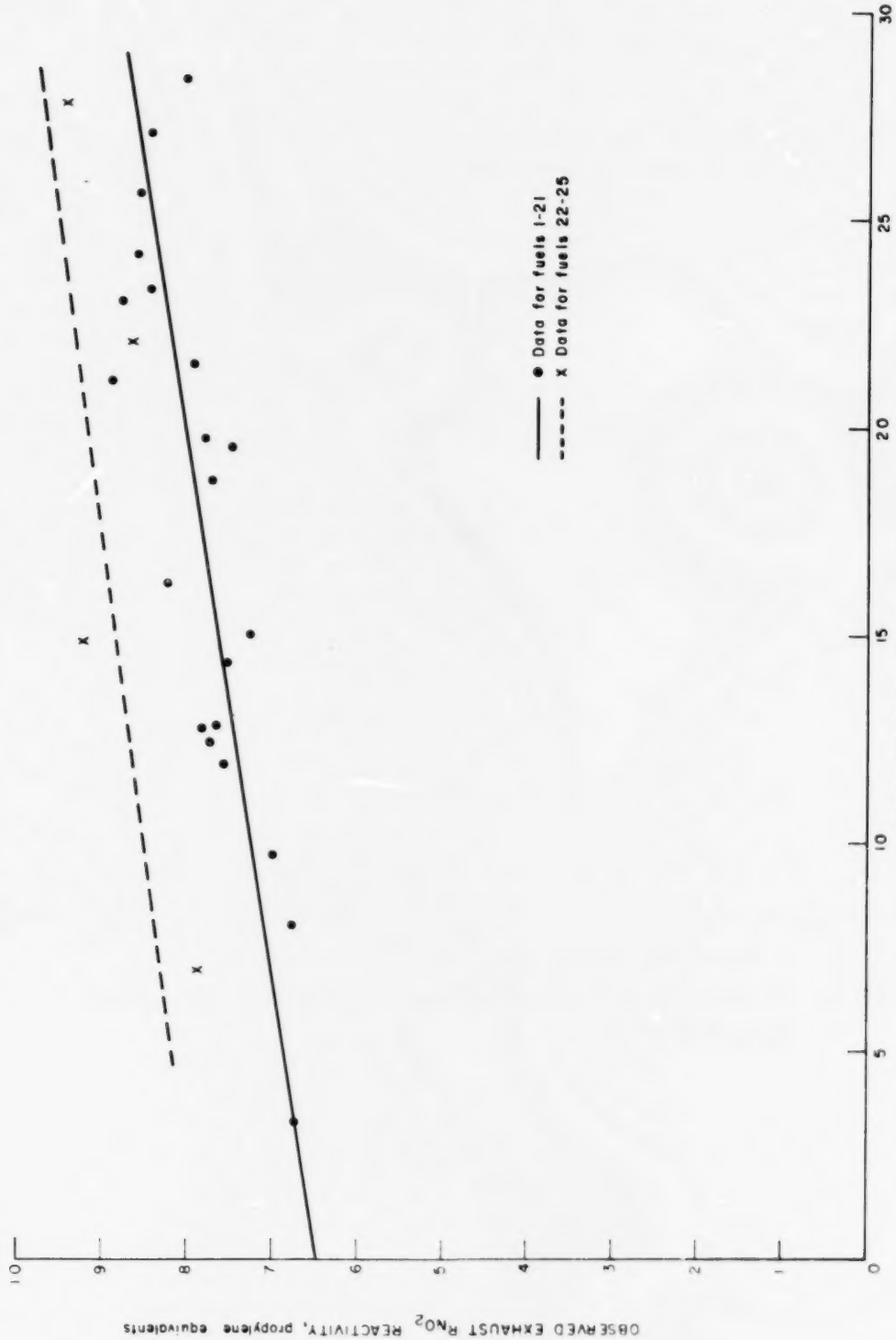
OBSERVED EXHAUST $R_{NO_2}$ REACTIVITY, propylene equivalents
POLYALKYLBENZENES IN FUEL, mole percent
● Data for fuels 1-21
x Data for fuels 22-25

FIGURE 5 - Correlation of Observed Exhaust Reactivities With Polyalkylbenzene Levels in Fuel.

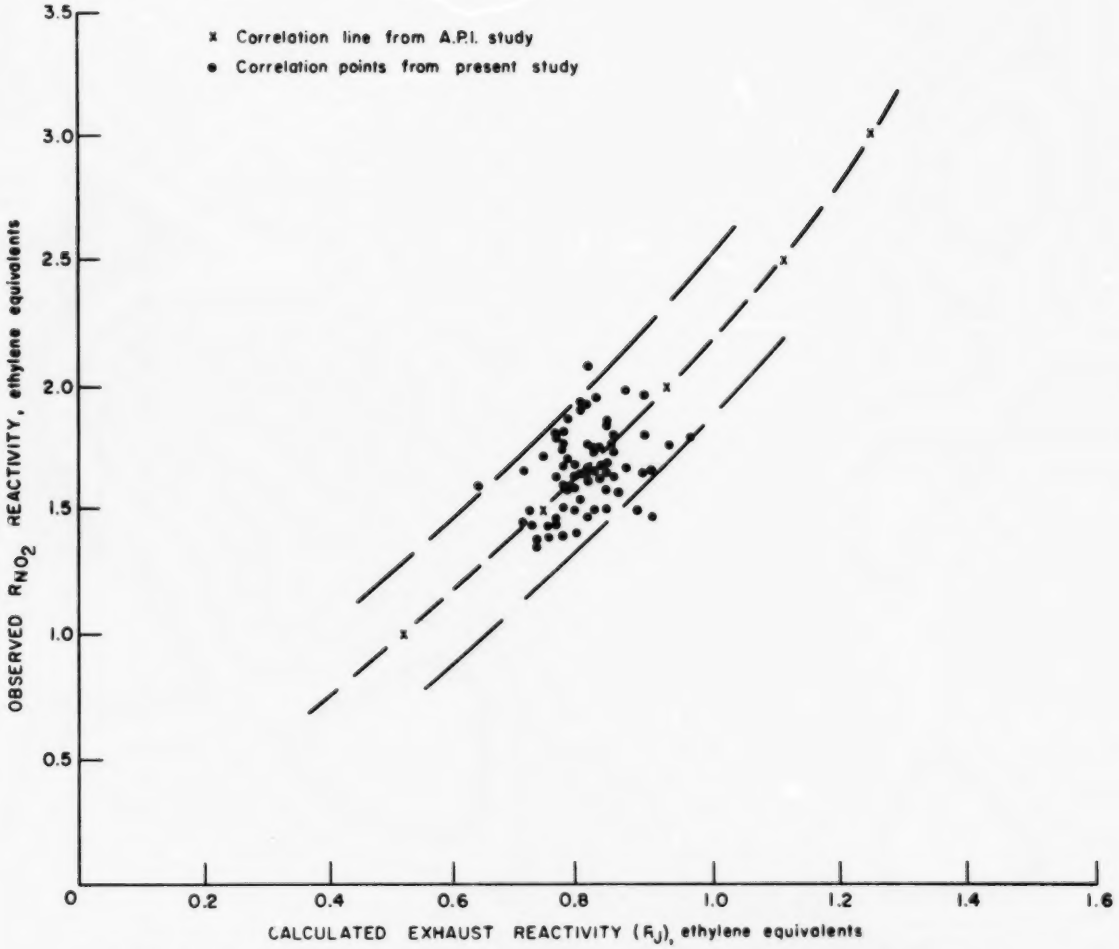


FIGURE 6.- Correlation of Observed and Calculated (Jackson Scale) Exhaust $R_{NO_2}$ Reactivities.

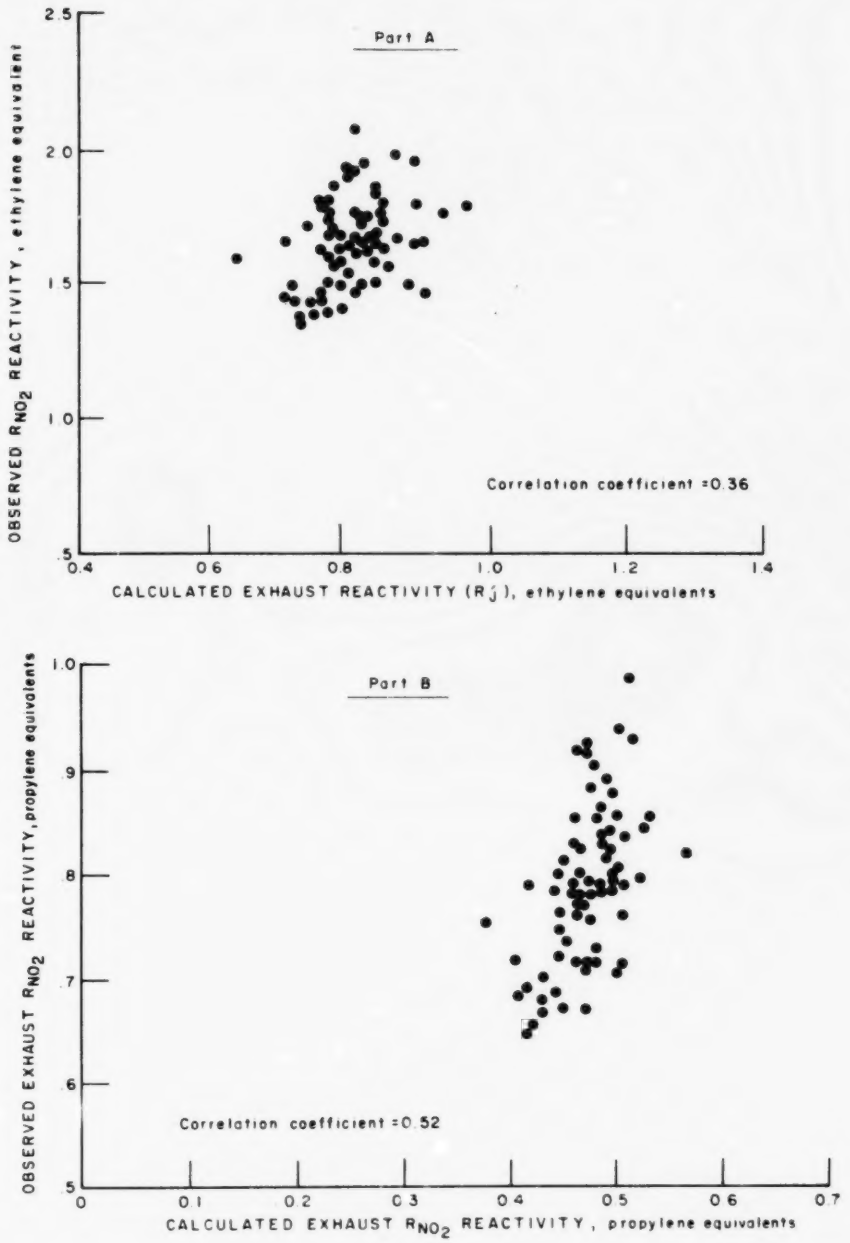


FIGURE 7.–Correlation of Observed Exhaust $R_{NO_2}$ Reactivities With Calculated Reactivities by Jackson and Bureau of Mines Scales.

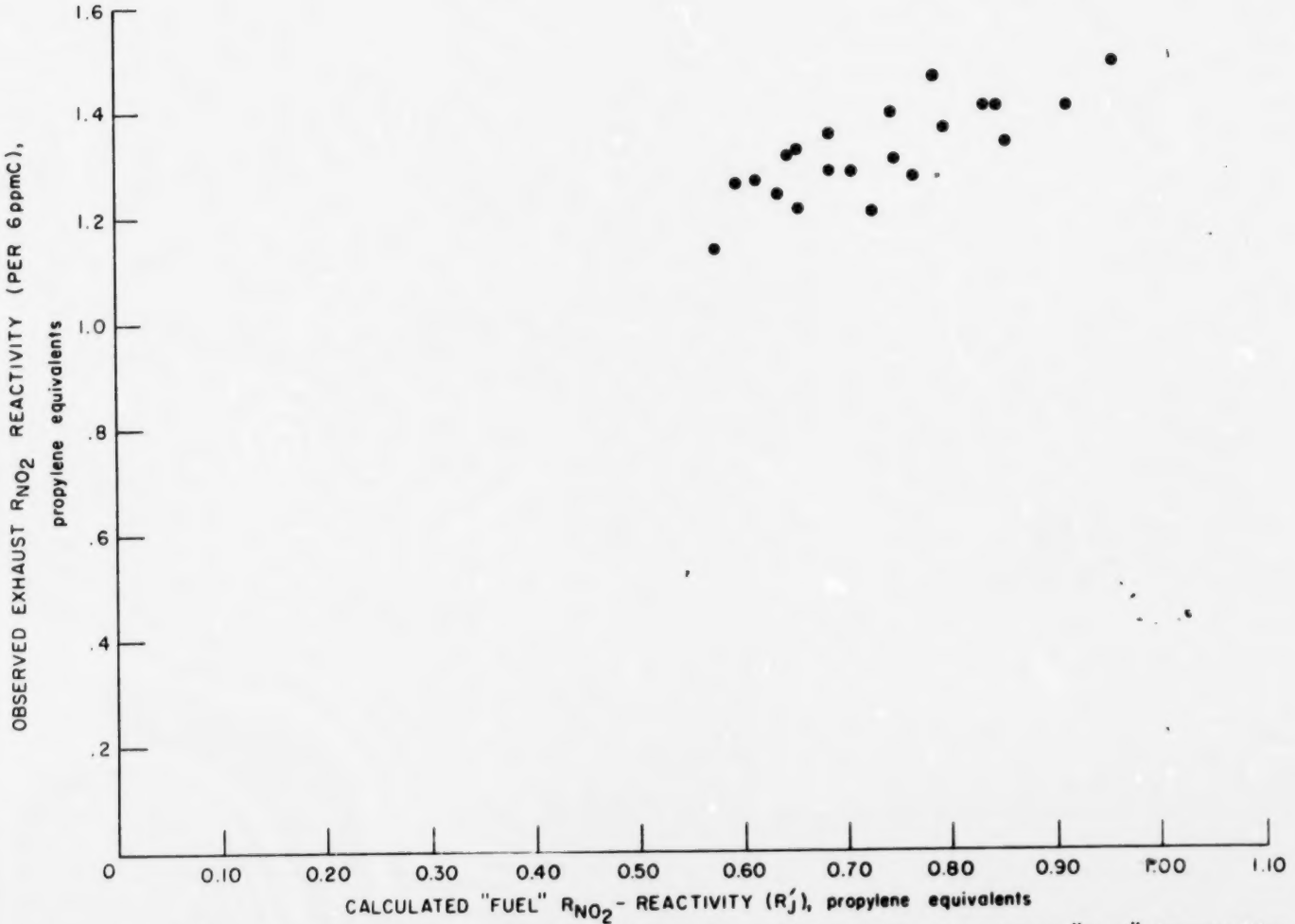


FIGURE 8.- Correlation of Observed Exhaust Reactivities With Calculated "Fuel" Reactivities.

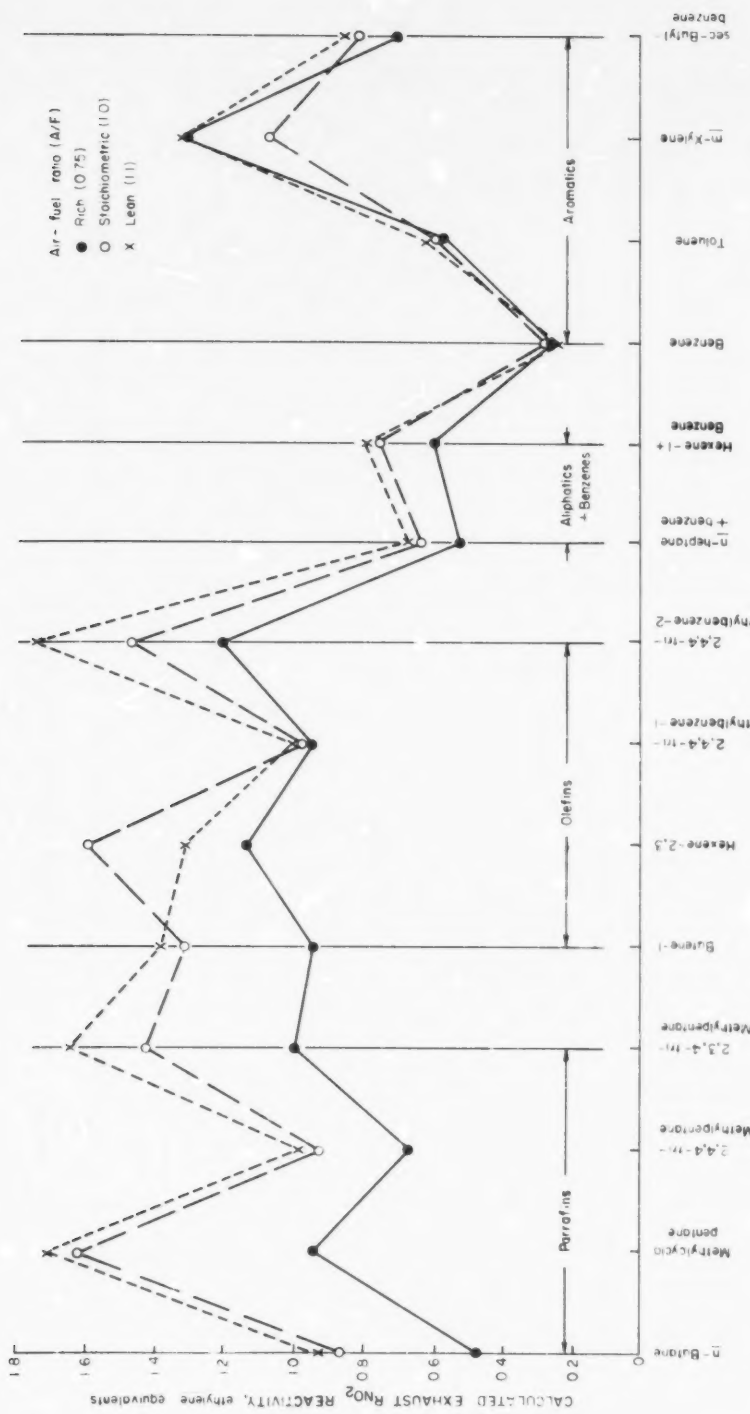


FIGURE 9.- Calculated $R_{NO_2}$ Reactivities of Exhaust From Simple Hydrocarbon Fuels Used Under Varied A/F Conditions.

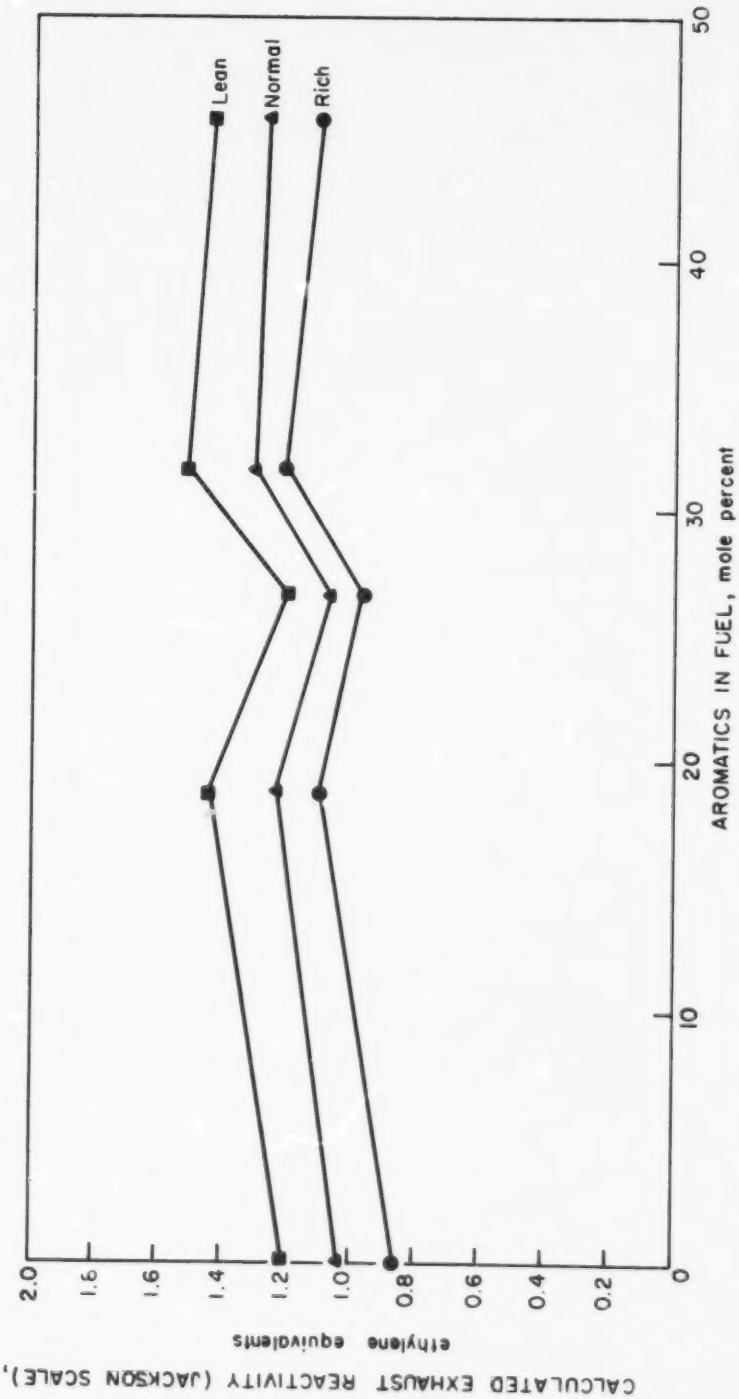


FIGURE 10.–Calculated $R_{NO_2}$ Reactivities of Exhaust From Gasoline Fuels Used Under Varied Air–Fuel Ratio Conditions.

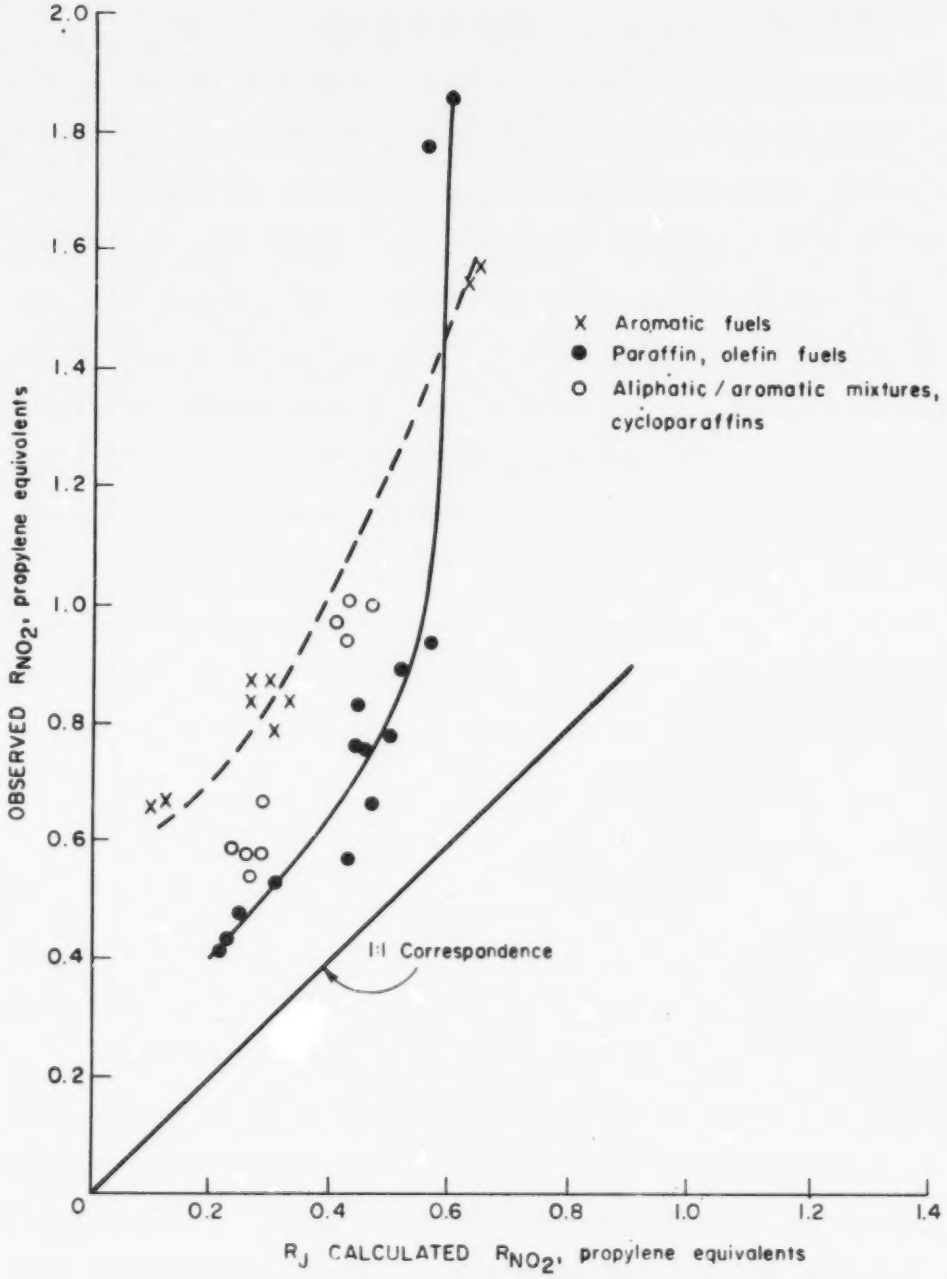


FIGURE 11.- Correlation of Observed and Calculated $R_{NO_2}$ Reactivities of Exhaust From Simple Hydrocarbon Fuels.

## APPENDIX A.--ANALYSIS OF EXHAUST MASS EMISSION DATA

The mass emission data for cars 5, 6, 7, 9, and 10 with fuels 12-21 were subjected to an analysis of variance to determine the importance of car effects, fuel effects, and car/fuel interactions on mass emission of hydrocarbon (HC), carbon monoxide (CO), nitric oxide (NO), formaldehyde (HCHO), and total aldehydes (TALD), and the effect upon total reactivity according to the Jackson scale (TRJ). A large car effect, significant at the 99.5 pct level, was found for each of the mass emission parameters. A much smaller fuel effect was observed although the effect was still significant at the 99.5 pct level for all parameters except CO which showed the fuel effect at the 90 pct confidence level. Car/fuel interactions were considered to be negligible as no effect was observed at a confidence level of 90 pct for any of the mass emission parameters. The car and fuel effects are depicted in figure A-1, where the bar for each car represents

FIGURE A-1. - Average emission levels for each car and each fuel.

an average over the ten fuels and the value for each fuel is an average over the five cars. It is clear that the car differences are indeed larger than the fuel differences for each of the mass emission parameters.

To further explore the fuel effects, the data for each fuel averaged over the five cars, summarized in table A-1, were correlated with thirteen fuel physical and chemical properties listed in table A-2. It should be noted that these thirteen fuel parameters are not all independent of each other. For example, specific gravity correlates well with 50 pct point and aromatic content. Thus, a correlation between mass emission data and

a fuel physical property may be the result of a relationship between the mass emission data and some chemical property of the fuel which also relates to the physical property. With this in mind, we turn our attention to the correlation analysis results which are summarized in table A-3. The HC mass emissions showed a high negative correlation with fuel 90 pct point and mole percent olefin and a fair positive correlation with fuel isoparaffin content and 10 pct point. Although the CO emissions did not correlate well with any of the fuel parameters, fair positive correlations were obtained with cycloparaffin content and paraffin content and fair negative correlations with olefin content and 90 pct point were observed. The NO emissions showed good positive correlations with specific gravity, 50 pct point, aromatic content and 90 pct point. Good negative correlations were observed for NO emissions with paraffin and isoparaffin contents. Formaldehyde and total aldehyde emissions correlated well with isoparaffin content and specific gravity. Formaldehyde emissions also correlated fairly well with aromatic content as did total aldehydes with cycloparaffin content. Total reactivity by the Jackson scale (TRJ) did not correlate well with any of the fuel parameters.

Regression models were chosen on the basis of the correlations discussed above. For those cases where fuel parameters correlated well with each other, only one of the parameters was included in the model. Also, in some of the models OLEF was replaced by PAR + AROM, and PAR was replaced by OLEF + AROM in order to give positive correlations since by definition OLEF + PAR + AROM = 100. Fuel parameters were deleted from the model when their coefficients were not significantly different from zero at the 95 pct confidence level. Results of the regression analysis are summarized in table A-4. Statistically significant models containing two independent

variables (fuel parameters) were obtained for CO and total aldehyde mass emissions. The models for the other four mass emission parameters reduced to the simple linear cases when all insignificant parameters were deleted. The final model for CO containing two fuel parameters (cycloparaffins and olefins, model CO-I) resulted in a correlation much improved over the best of the simple correlations (model CO-II, table A-4) as can be seen by the squares of the correlation coefficients (0.798 versus 0.392). A much smaller improvement resulted from the two parameter models for total aldehydes (0.915 versus 0.824). The best of the simple correlations (one parameter model) for each of the six exhaust mass emission parameters are illustrated in the graphs in figure A-2.

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FIGURE A-2. - Variation of exhaust mass emission parameters with various fuel composition parameters.

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In brief, correlations between exhaust mass emissions and fuel composition were obtained in all cases. Those for formaldehyde and for total reactivity-Jackson Scale may be questionable; the others appear to be fully valid for the sets of fuels and vehicles tested. Although useful as indicators, the correlations obtained in the study may not be reliable in extension to a much broader population of fuels and engines. In this respect it is noteworthy that only relatively small fuel effects were observed despite the great diversity in composition in this set of fuels. For the five cars, the car differences have a far greater impact upon exhaust emission levels than do fuel differences.

TABLE A-1. - Summary of mass emission data for five cars and ten fuels

| Fuel | Mass emission parameter | | | | | |
|---|---|---|---|---|---|---|
| | HC[1/] | CO | NO | HCHO | TALD | TRJ |
| 12 | 25.6 | 353 | 43.0 | 0.677 | 1.186 | 13.5 |
| 13 | 26.6 | 362 | 41.2 | .656 | 1.126 | 12.9 |
| 14 | 26.7 | 355 | 40.8 | .708 | 1.123 | 15.1 |
| 15 | 27.3 | 357 | 46.2 | .597 | 1.072 | 12.3 |
| 16 | 28.5 | 358 | 40.8 | .700 | 1.285 | 13.4 |
| 17 | 24.2 | 333 | 46.8 | .685 | 1.097 | 13.3 |
| 18 | 27.9 | 363 | 44.4 | .590 | 1.107 | 11.6 |
| 19 | 25.4 | 374 | 43.9 | .595 | .946 | 12.4 |
| 20 | 24.6 | 350 | 42.6 | .633 | 1.124 | 12.7 |
| 21 | 25.4 | 350 | 46.2 | .591 | 1.077 | 12.3 |

1/All values are averages over triplicate tests with each of five cars expressed as grams/test except for TRJ which is expressed as (grams ethylene)/test.

TABLE A-2. - List of fuel physical and compositional properties used in correlations

| | |
|---|---|
| 1. | Reid Vapor Pressure (RVP) |
| 2. | Specific Gravity (Sp.Gr.) |
| 3. | 10 pct point in °F (10%P) |
| 4. | 50 pct point in °F (50%P) |
| 5. | 90 pct point in °F (90%P) |
| 6. | Mole pct paraffin (PAR) |
| 7. | Mole " olefin (OLEF) |
| 8. | Mole " aromatic (AROM) |
| 9. | Mole " monoalkylbenzenes (MonoAlkBz) |
| 10. | Mole " polyalkylbenzenes (PolyAlkBz) |
| 11. | Mole " n-paraffins (n-Par) |
| 12. | Mole " isoparaffins (iso-Par) |
| 13. | Mole " cycloparaffins (cyclo-Par) |

TABLE A-3. - Correlation coefficients for exhaust mass emission levels and fuel physical and compositional properties

| | HC | CO | NO | HCHO | TALD | TRJ |
|---|---|---|---|---|---|---|
| RVP..... | -0.557 | -0.291 | -0.044 | -0.051 | -0.016 | -0.077 |
| Sp.Gr..... | - .241 | - .033 | .856 | - .703 | - .746 | - .483 |
| 10%P..... | .500 | .231 | .300 | - .180 | - .108 | - .142 |
| 50%P..... | - .238 | - .387 | .797 | - .433 | - .484 | - .208 |
| 90%P..... | - .823 | - .629 | .607 | - .002 | - .471 | .156 |
| PAR..... | .373 | .509 | - .856 | .437 | .423 | .348 |
| OLEF..... | - .856 | - .626 | .313 | .290 | - .316 | .358 |
| AROM..... | .161 | - .142 | .711 | - .654 | - .242 | - .603 |
| MonoAlkBz.. | .281 | .228 | .199 | - .467 | - .099 | - .647 |
| PolyAlkBz.. | .013 | - .240 | .437 | - .213 | - .240 | .116 |
| n-Par..... | - .484 | - .301 | - .274 | - .393 | - .203 | - .332 |
| iso-Par.... | .612 | .052 | - .782 | .708 | .908 | .495 |
| cyclo-Par.. | - .258 | .568 | .098 | - .367 | - .733 | - .189 |

TABLE A-4. - Summary of regression analysis results

| Exhaust mass emission parameter (dependent variable) | Model No. | Fuel parameter (independent variable) | Estimate of coefficient | Standard error of estimate of coefficient | t-value for coefficient | Regression constant | Square of multiple correlation coefficient |
|---|---|---|---|---|---|---|---|
| HC | I | 1/10% P | 2/ - | | | | |
| | | 90% P | -0.0521 | 0.0127 | -4.10 | 40.9 | 0.678 |
| | | iso-Par | - | | | | |
| | II | (PAR + AROM) | 0.217 | 0.0456 | 4.76 | 6.27 | 0.739 |
| CO | I | cyclo-Par | 0.745 | 0.199 | 3.76 | 362 | 0.798 |
| | | OLEF | -1.328 | .327 | 4.06 | | |
| | | PAR | - | | | | |
| | II | (PAR + AROM) | 1.189 | 0.532 | 2.23 | 246 | 0.384 |
| NO | I | (OLEF + AROM) | 0.213 | 0.046 | 4.61 | 34.0 | 0.726 |
| | | 90% P | - | | | | |
| | | iso-Par | - | | | | |
| HCHO | I | AROM | - | | | | |
| | | iso-Par | 0.00270 | 0.00095 | 2.84 | 0.570 | 0.502 |
| TALD | I | iso-Par | 0.00494 | 0.00089 | 5.56 | 1.000 | 0.915 |
| | | cyclo-Par | - .00332 | .00122 | -2.73 | | |
| | II | iso-Par | 0.00621 | 0.00102 | 6.11 | 0.947 | 0.824 |
| TRJ | I | AROM | - | | | | |
| | | MonoAlkBz | -0.0763 | 0.0318 | -2.40 | 14.2 | 0.418 |
| | | iso-Par | - | | | | |

1/Abbreviation of parameters are listed in table A-1.
2/The dash indicates the parameter was dropped from the model because its coefficient was not significantly different from zero at the 95 pct confidence level.

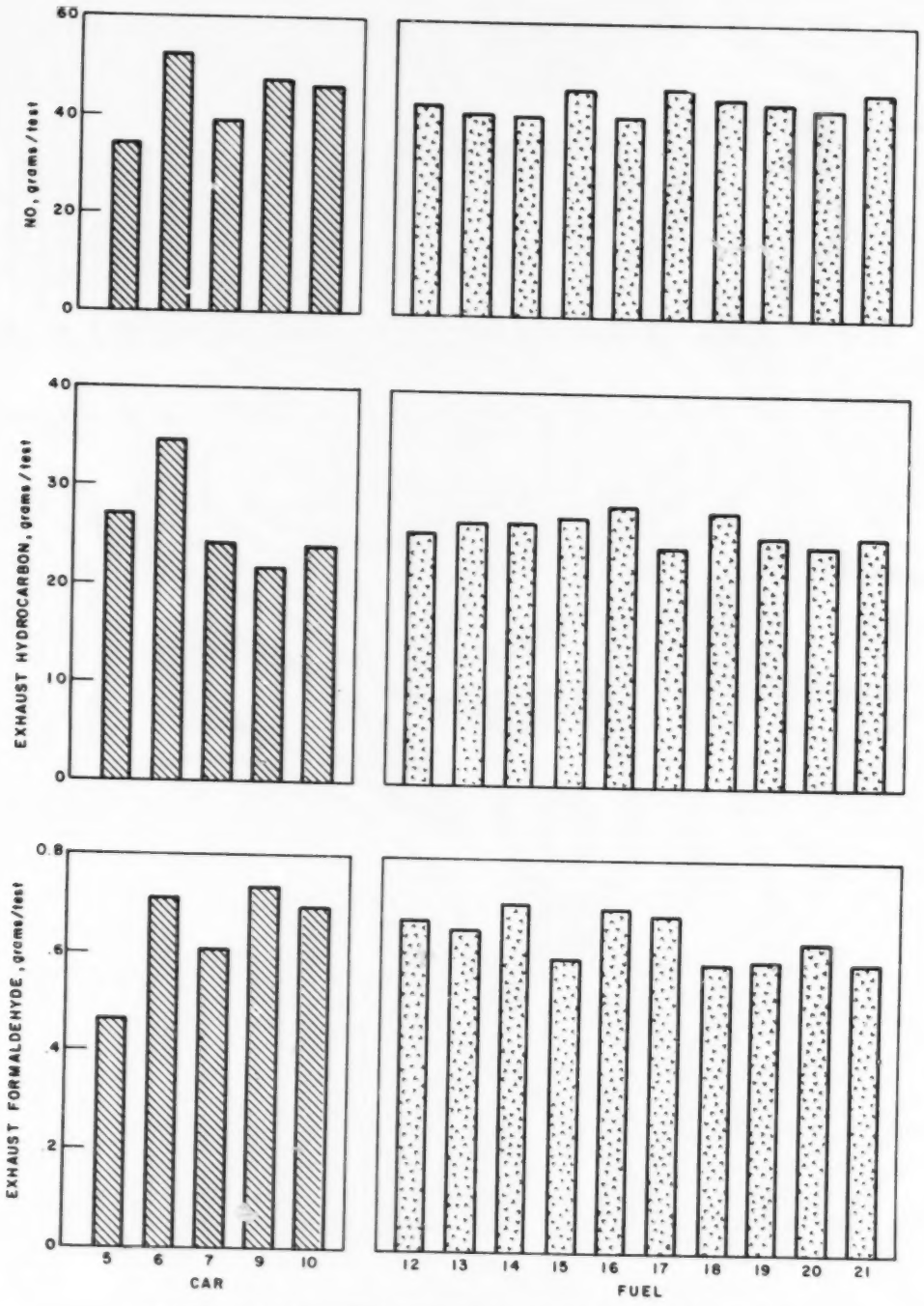


FIGURE A-1.-Average Emmision Levels for Each Car and Each Fuel.

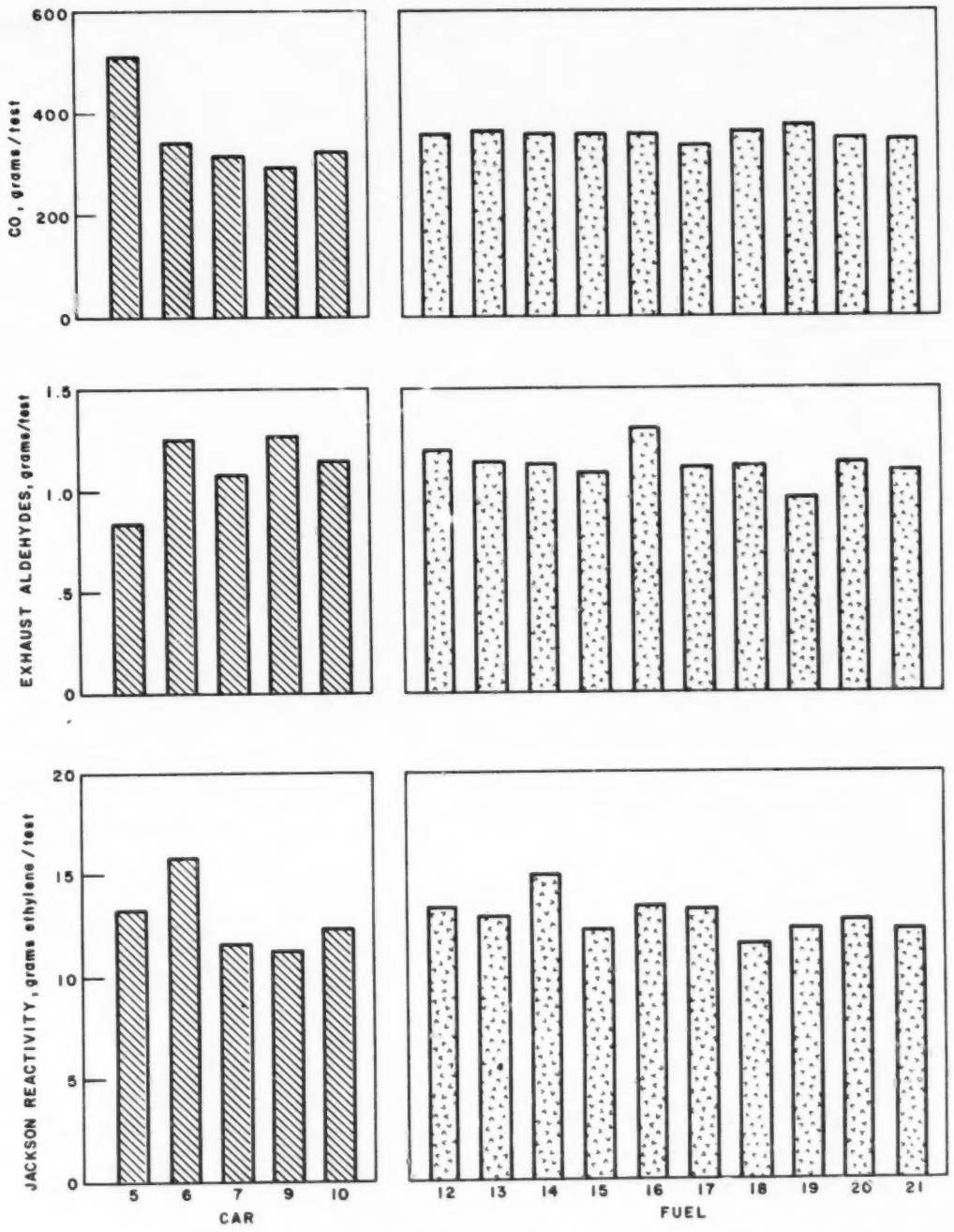


FIGURE A-1.-Average Emmision Levels for Each Car and Each Fuel (continued)

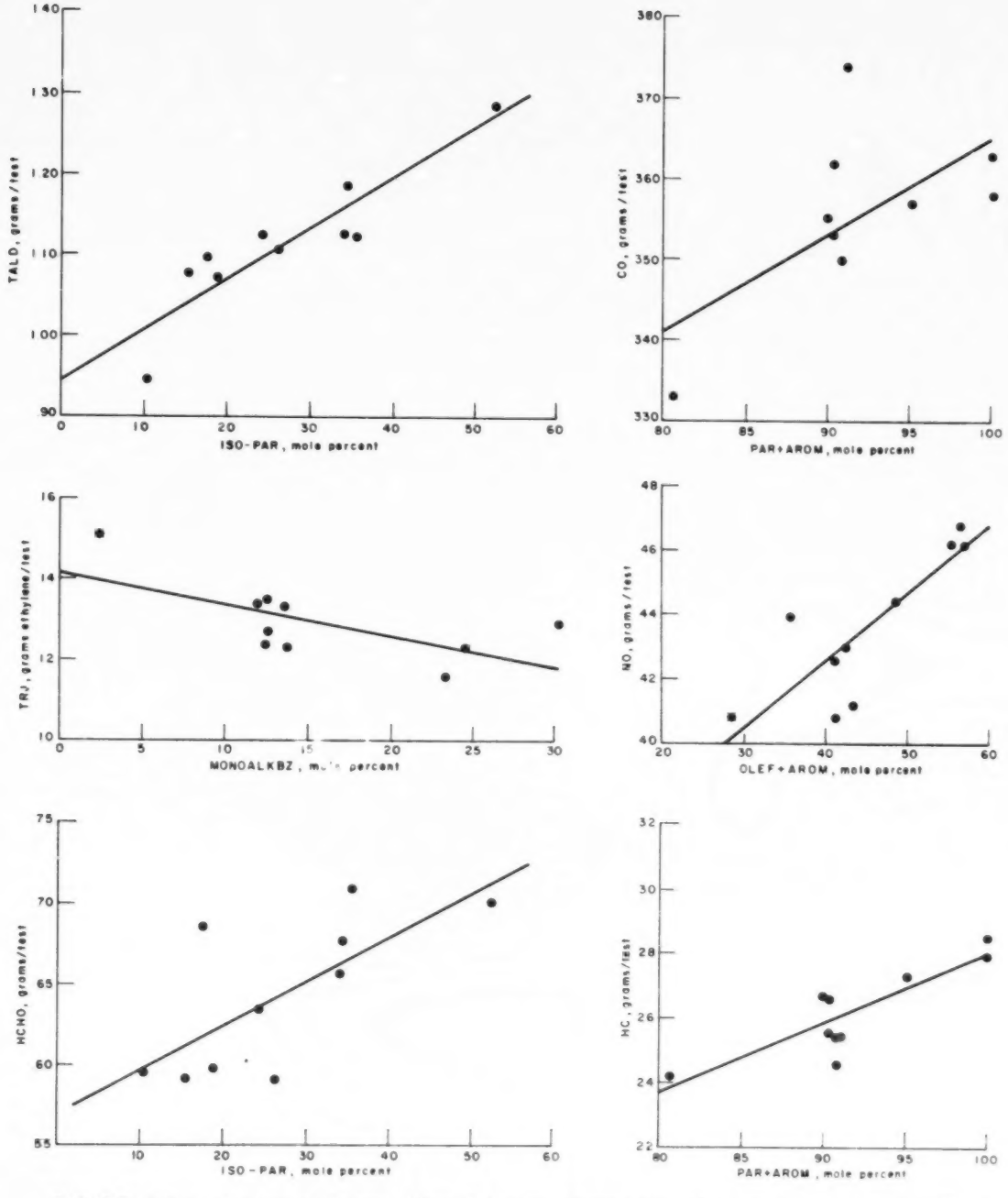


FIGURE A-2.- Variation of Exhaust Mass Emission Parameters With Various Fuel Composition Parameters.

Final report for the Bureau of Mines-EPA
cooperative research project
"Characteristics and Photochemical
Reactivity of Emissions"

## PART II. TOXIC PRODUCTS FROM FUEL ADDITIVES

### INTRODUCTION

Under provisions of legislature now in effect, the Environmental Protection Agency (EPA) has a responsibility to control the use of fuel additives wherein such use might have an adverse effect in automotive emissions or emission control systems. One possible regulatory course is to require any manufacturer or user of an additive to provide data on additive effects as related to emissions. These data would necessarily be obtained using a standardized test procedure specified or approved by EPA. No such procedure now exists and this work was authorized by EPA as a first effort toward developing one part of a test procedure to measure additive effects on emission.

Much has been published on the combustion of hydrocarbons (1), but very little is known of the fate of gasoline additives in the combustion process and, as indicated above, analytical procedures for the additive-derived products are non-existent. Thus, this research reported upon is a first effort in the experimental development of the required analytical procedures. More specifically, procedures were sought for the determination of toxic gaseous products, if any, resulting from thermochemical reactions of fuel additives in the combustion process. The general approach was to operate an engine using additive-free fuel to obtain reference data on exhaust hydrocarbon and oxygenate composition; this was followed by tests in which the engine was operated using the same fuel except with additive. The exhaust analyses included hydrocarbon and oxygenates determination together with analysis for the additive and for its direct combustion products in the gaseous portion of the exhaust.

To place this report in proper context, it should be noted that it covers essentially nothing more than the preparatory phase of an experimental study with total effort not exceeding about one-half man year. The work was done solely to provide guidance in selection of analytical methods for consideration and was not intended to provide definitive information on additive effects, per se.

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## EXPERIMENTAL PROCEDURES AND RESULTS

Preliminary experiments to identify products from one fuel additive were conducted using a single-cylinder research engine. The fuels used were isooctane and isooctane with methyldiphenylphosphate (MDP) additive at a level of 3.624 grams per gallon (corresponding to two theories based on 2 cc TEL per gallon). Exhaust samples were analyzed for phosphorous compounds with a Micro Tek GC-2500R gas chromatograph equipped with a flame photometric phosphorous detector (also from Micro Tek) and a 4-ft glass column with 3 pct OV 101 on Gas Chrom Q at a temperature of 160° C. Earlier experiments had shown this column to be superior to a 6-ft glass, 3 pct OV 101 on Gas Chrom Q column. The three samples analyzed for phosphorous were (1) exhaust gas prediluted with nitrogen to prevent condensation of water, (2) condensate from raw exhaust passed through a trap at 0° C, and (3) the exhaust gas which passed through the 0° C trap.

No phosphorous compound was detected in any of the samples from the pure isooctane runs. Also, no phosphorous compound was detected in the gaseous samples from the tests using isooctane without additive; however, the condensate chromatograms showed two, and occasionally three, peaks. Two of these peaks matched the retention times of the peaks obtained when a dilute solution of the additive itself was chromatographed. Therefore, it was concluded that part of the fuel additive escaped combustion and passed into the exhaust unburned. This unburned additive in the exhaust was estimated, from the chromatographic data, to be less than 1 pct of the amount in the fuel.

In a subsequent run using pure isooctane fuel, phosphorous compounds were detected in the condensate sample suggesting that additive-derived products deposit in the engine-exhaust system causing memory effects.

Because the combustion system of the single-cylinder research engine is not representative of automotive equipment, a second engine was selected for additional exploratory work. This engine, an Onan, 2-cylinder, four cycle, 49.8 cubic-inch displacement (CID) model was judged to provide a combustion environment closely approaching that of an automotive engine in medium duty service. After engine break-in, several tests were run using an additive-free gasoline to compare hydrocarbon composition of exhaust from this engine with composition of exhaust from four commercial passenger automobiles The Onan exhaust composition was found to be somewhat different from that of the automobile exhaust as shown in table 13, but the similarity was close enough that its exhaust was believed suitable for purposes of analytical method development in the context of a preparatory study.

TABLE 13.- Comparative exhaust hydrocarbon composition from Onan engine and as determined for four automotive engines 1/

| Compound | HC composition, mole pct | |
|---|---|---|
| | Onan engine | Range for four auto engines |
| Paraffins | 34.4 | 25.7--33.0 |
| Olefins | 16.6 | 27.0--35.6 |
| Aromatics | 36.6 | 25.0--31.0 |
| Methane | 18.2 | 11.1--18.9 |
| Acetylenes | 13.4 | 9.9--13.7 |

1/ All tests made using identical fuels.

Concurrent with the experiments using the single-cylinder and Onan engines, work was begun on the procedures for oxygenate analysis. The initial phase of this development involved preparation of two calibration blends of mixed oxygenates and preparation of porous polymer packed beds for collection of samples. Familiarization with the analytical equipment and techniques was accomplished using the calibration blends. Initial attempts to analyze samples from the engine runs were not successful presumably due to insufficient sample. This problem was not explored further because of an interruption in the program and the subsequent decision to use a full-boiling range gasoline in an automobile engine, thereby making detailed oxygenate analysis impossible with available techniques.

The work reported just above was done in the second quarter of FY 72. Because funds were lacking to sustain an experimental program throughout the last three quarters, the program was interrupted to await availability of a test engine specified by the EPA project monitor. The experimental program subsequently was resumed in the last quarter using a 350-CID 1971 Chevrolet engine. Prior to its use in the tests, the engine was partially dismantled and the valves, cylinders, and pistons cleaned thoroughly. The engine was reassembled on a dynamometer test stand with a completely new exhaust system including new exhaust manifolds, muffler, and exhaust pipe up to the sample port section. This section was cleaned thoroughly using Skasol, water, and acetone. All sample lines in the proportional sampler, used to obtain exhaust sample, were cleaned or replaced. The engine was then run for several hours using an additive-free gasoline and adjusted to manufacturer's specifications. The motor oil used was Havoline Super Premium 10W40.

Concurrent with the engine preparation, analytical development continued with evaluation of various chromatography columns and temperature conditions for determination of two commonly used phosphorous additives, tricresylphosphate (TCP) and MDP using the phosphorous-specific flame photometric detector.

Analysis for TCP was difficult due in part to the extremely low vapor pressure of TCP. Several different stainless steel columns were used; these were:

1. A 12-ft x 0.010-inch column dynamically coated with a 10 pct solution of SE-30 in methylene chloride.
2. A 6-ft x 0.010-inch uncoated column.
3. A 6-ft x 0.010-inch column coated with an 0.8 pct solution of OV-17.
4. A 6-ft x 0.020-inch column coated with a 5 pct solution of OV-17.

5. A 6-ft x 0.020-inch column coated with a 10 pct solution of OV-17.

6. A 14-ft x 0.020-inch column coated with a 5 pct OV-17 solution.

7. A 30-ft x 0.020-inch column coated with a 5 pct OV-17 solution.

8. A 4-ft x 1/8-inch column with 4 pct HIEFF-BP on 60/80 mesh, acid washed, DMCS treated Chromosorb G.

Carrier gas flow and column temperature were varied for each column to search for optimum sensitivity, peak shape, and retention time. The best results for TCP left much to be desired. With the 14-ft x 0.020-inch 5 pct OV-17 column at 270° C with a carrier flow of 50 cc/min, a 0.5 µl injection of a 10 ppm solution of TCP in methanol produced a 3-inch peak with considerable tailing at a retention time of 0.5 minute. Considering the instrument noise and the poor quality of the peak, the limit of detection would be about 1 to 2 ppm TCP with these conditions.

Analysis for MDP showed much more promise as easily interpretable peaks were obtained with several of the columns. With the 14-ft x 0.020-inch, 5 pct OV-17 column for example, two peaks with retention times of 0.25 and 1.3 min were obtained using a column temperature of 140° C and a carrier flow of 95 cc/min. The response for the second peak was about 2.4 inch per ppm for a 1 µl injection of a 100 ppm solution of MDP in methanol calculated for the most sensitive instrument settings. Acceptable results were obtained also with the 4 pct HIEFF-BP column at a temperature of 220° C and a carrier flow of 80 cc/min. Response for the second of two peaks (retention times 0.6 and 2.8 minutes) was about 1.8-inch per ppm for a 1 µl injection of the 100 ppm MDP solution.

Prior to the time that tests were run using the 350-CID engine, the project directors (EPA) directed that work with the phosphorous additives be discontinued and effort directed toward methylcyclopentadienyl manganese tricarbonyl and polybutene amine F-310. Work was begun on analytical procedures for organic manganese compound determination using gas chromatography and flame photometry. No definitive results were obtained in the short time that remained in FY 72.

## REFERENCES

1. For example see

   (a) Fleming, R. D. Effect of Fuel Composition on Exhaust Emissions From a Spark-Ignition Engine. Bureau of Mines Report of Investigations 7423, 1970, 68 pp.

   (b) Morris, W. E. and K. T. Dishart. The Influence of Vehicle Emission Control Systems on the Relationship Between Gasoline and Vehicle Exhaust Hydrocarbon Composition. Effect of Automotive Emission Requirements on Gasoline Characteristics, ASTM STP 487. American Society for Testing and Materials, 1971, pp. 63-101.

Final report for the Bureau of Mines-EPA
cooperative research project
"Characteristics and Photochemical
Reactivity of Emissions"

# PART III. - DIESEL ODOR

## INTRODUCTION

The initial objectives for work during the past year were isolation, fractionation, and reconstitution of diesel odorants, particularly the unstable and reactive materials. For convenience in exhaust handling and odor measurements the materials to be examined were grouped as either those retained in water scrubbed (0° C) samples or as those passing a water scrubber.

There were three major problems to be considered in carrying out this program. They were:

1. Development of an odorant dilution and presentation system suitable for use with isolated exhaust components and synthetic odorants.

2. Establishing methods for demonstrating reactivity and stability characteristics of diesel exhaust odorants. These demonstrations were based on odor measurements of exhaust that was treated for removal of specific classes of compounds or for decomposition of unstable materials.

3. Isolation and collection of unstable components. As far as possible these materials were to be examined for odor contribution based on samples obtained from exhaust.

In addition to work undertaken for the objectives above, a report was prepared and published on previous work. This report covered a study to quantify the contribution to diesel exhaust odor of: (1) carbonyl compounds, (2) phenols, and (3) hydrocarbons 1/.

## EXPERIMENTAL

### Odor Determination

Odor evaluations were made by a trained panel using the Turk 2/ odor rating method. This was the procedure used in previous studies 1/.

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1/James W. Vogh. BuMines Rept. of Inv. No. 7632 (1972), 11 pp.
2/Amos Turk. P.H.S. Publ. No. 999-AP-32, Washington, D.C. (1967).

## Odorant Dilution Systems

### Chamber Dilution

A metal and glass chamber that had been used in photochemical studies was modified to permit the presentation of diluted exhaust and odorant for odor evaluation. Samples (either gas or liquid) were introduced into the chamber in amounts calculated to give the desired concentration or dilution ratio on the basis of the total volume of the chamber. The diluted sample in the chamber was forced out through a sniff port by inflating a Tedlar film bag that was contained in the chamber. The chamber was found to have a strong background odor. This odor approached the intensity of diluted (100:1) diesel exhaust and it appeared to be too strong to eliminate its contribution to the total odor by background odor measurements. Thorough cleaning of the interior of the chamber eliminated the odor for a short period. The rapid return of odor to its original level interfered with use of the chamber as a dilution system and no further experimental work was done using this system.

A second system for odorant dilution was based on a large Teflon film bag (about 200 liters volume) with a stainless-steel bellows pump (Metal Bellows Corp., model MB-155) for delivery of the sample to a sniff tube. The dilution air was introduced into the bag prior to and during the odorant sample introduction in such manner as to promote rapid mixing. Flow rate and duration of flow both for diluent air and for the odorant sample were measured to establish the dilution ratio. The diluent air was passed through activated charcoal at 0° C and through distilled water at 15° C before entering the bag. At the end of introduction of the air and odorant sample, the bag was kneaded about 20 seconds to complete the mixing. In some odor evaluation work the bellows pump was replaced by a press composed of a plywood sheet and sufficient weights to obtain the desired flow out the sniff tube.

The third system for odorant dilution was a modification of the syringe fed dilution device used in previous odorant studies 1/. The changes permitted the syringe delivery rate to be adjusted so that it could be used with exhaust samples. Diluent air for the tests was passed through charcoal and water as described above.

## Odorant Reaction and Aging

Exhaust scrubbing and presentation of the treated exhaust was carried out by procedures used previously 3/. The procedure involved use of a liquid lift scrubber at 0° C containing 15 ml of water or solution and an exhaust or gas flow of 4.5 liters per minute. In addition to the special attention given to water scrubbing of exhaust, certain reagent solutions were used. They were:

1. Sodium sulfite solution. This solution was used at 1.0 molar concentration. With this and the other reagent solutions odor evaluations were made after passing exhaust through the solution for four minutes.

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3/J. W. Vogh. J. Air Poll. Control Assoc., 19, 773 (1969).

2. Morpholine solution. This solution was prepared at a concentration of 1.7 molar morpholine and 0.9 normal acetic acid or benzoic acid in water. In a few runs diethanolamine was used instead of morpholine.

3. Potassium permanganate solution. This was used at concentration of 0.2 molar $KM_nO_4$ with 0.33 molar $H_2SO_4$.

4. Hydroxylamine solution. Used at 0.5 molar $NH_2OH$ and 0.5 molar $NH_2OH$ x HCl. This reagent has been examined previously 3/ for its effect on diesel odor.

All of these solutions were evaluated for their effectiveness in removing selected components from gas streams. The evaluation method has been described 3/. Trial components tested in gas blends were ketene, ethyl hydroperoxide, propylene oxide, methyl acrylate, vinyl propionate, and allyl propionate.

A series of runs were made for evaluation of odor changes in exhaust due to aging at room temperature. This procedure was based on holding an exhaust sample in a glass pipe section of the odor evaluation system for a measured period before mixing into the dilution air stream. The glass pipe was 2.6 cubic I.D. and had a retention volume of 2200 cc. It was covered with aluminum foil to prevent entrance of light. Contents of this glass pipe volume were drawn out by an air aspirator to be mixed into the carrier stream. This was accomplished by use of a pair of three way valves positioned so as to permit gas flow either through the glass pipe or through a small bypass. If the contents of the glass pipe were displaced from it in strictly plug flow it would have provided uniform samples for about 29 seconds. However, measurement of a synthetic sample out a side stream indicated that a uniform sample (that is, unmixed with displacement air) could be obtained only for about 22-25 seconds. This determination was accomplished by use of an organic vapor blend displaced by clean air with the side stream led directly to the flame ionization detector of a gas chromatograph. Because plug flow was not achieved, odor measurements were limited to the 15 second period immediately after the start of mixing the aged sample into the carrier gas stream.

## Analytical Methods Development

Preliminary studies were carried out on detection of organic hydroperoxides by gas chromatographic methods. Organic hydroperoxides were prepared for use in development of the chromatographic method. The synthesis method generally used was based on oxidation of the magnesium or zinc organo metallic compounds 4,5/. Ethyl, n-propyl, isopropyl, allyl, and benzyl hydroperoxides were prepared. Chromatographic columns used were either the all glass packed columns with UCON 50-HB5100 or Carbowax 20M used for oxime chromatography 6/ or glass capillaries coated with the same liquid phases. Hydroperoxides in synthetic samples and in water through which

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4/H. Hock and F. Ernst. Chem. Ber., 92, 2716-2723 (1959).
5/H. E. Seyforth, J. Henkel, and A. Rieche. Angew. Chem., Intern. Ed., 4, 1074 (1965).
6/J. W. Vogh. Anal Chem., 43, 1618 (1971).

exhaust had been passed were isolated by extraction of the neutral materials with an organic solvent such as pentane or benzene after the solution had been made basic with sodium hydroxide. The hydroperoxides were then recovered from the neutralized solution by extraction with ethyl ether. This is a common procedure for hydroperoxide isolation and purification 7/.

## RESULTS AND DISCUSSION

### Odor Presentation

Earlier work in odor evaluation of synthetic odorants and isolated exhaust fractions had been based on dilution by a carrier gas stream of samples held in a gas syringe 1/. While this procedure served well for the determinations that were made in the previous work there were some doubts concerning its suitability in study of other diesel exhaust odorants. The primary difficulty appeared to be the loss of odorants in samples obtained from exhaust trapped on porous polymer (Chromosorb 102) type beds. However, information 8/ obtained later indicated that diesel odorants could not be recovered from the porous polymer by the methods used previously.

The chamber dilution method offered certain advantages such as accurate and rapid dilution and large enough sample volume to allow repeated odor evaluation of a single sample. However, the chamber had a strong background odor that could not be removed by scouring and solvent washing. The odor became more intense when the chamber air was humidified, possibly indicating displacement of adsorbed odorants from the walls. Although some exhaust samples were introduced into the chamber, no useful odor evaluation results were obtained.

The odorant dilution system based on the Teflon film did not present any problems in background odor. In odor evaluation measurements using n-propyl propionate as a test material, the same odor intensities were observed at the same dilution level in this system and in the dynamic flow system used in direct exhaust odor evaluation. However, odor intensity of diluted exhaust that had been passed through a scrubber was much lower than expected in comparison with the same exhaust in the dynamic dilution system. Rough estimates on odorant levels indicated that of the amounts originally present, 60-90 pct had disappeared by the time the diluted exhaust was pumped out the sniff tube. The greatest losses occurred for exhaust produced at full load operation. It was noted by the odor panelists that the air pumped out of the Teflon bag by the stainless steel bellows pump was somewhat heated (by compression and by heat transferred from the pump body). Since it seemed possible that this heating might cause destruction of unstable odorants, the pump was replaced with the large bag press previously described. However, no improvement in exhaust odor level was found.

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7/A. G. Davies. "Organic Peroxides," Butterworth & Co., London, 1961, pp. 114.

8/A. D. Little, Inc. Report, "Analysis of the Odorous Compounds in Diesel Engine Exhaust," CRC Project CAPE-7-68, Report No. ADL 73686-1, September 16, 1971, 22 pp.

At this point it was not established whether the loss of odor was due to absorption in the bag or to chemical deterioration of the odorants during the time required for sample introduction, mixing, and presentation for odor rating. The syringe fed dilution device had the advantage of more rapid sample handling and presentation. This sampling procedure was examined in a series combined with exhaust aging measurements. Results are shown in table 14. In this study, exhaust that had been passed through a cold water scrubber was drawn into the syringe and then delivered into the carrier stream. The odor values given under "direct" sampling refer to exhaust passed directly into the dynamic dilution system and are taken as the reference values for odor intensity measurements. Engine difficulties prevented completion of this study under full load conditions. However, results at no load operation indicate a serious loss of exhaust odorants and would limit the use of this sampling method to qualitative odor evaluation unless the loss of specific odorants could be determined.

It is possible that some of the loss in odor intensity with syringe sampling may have been due to adsorption and conditioning problems. The adsorption of odorants on the relatively limited interior surface of the syringe would cause more serious loss at low concentrations found in exhaust than it would in samples prepared from exhaust by concentration and isolation techniques. At higher concentrations the adsorptive capacity of the syringe wall would become saturated. The conditioning problem arises in the very rapid delivery of exhaust from the syringe required to present the 100:1 dilution to the panelists. This prevents the proper conditioning of sample lines up to the sniff port. On the other hand, a more concentrated sample in the sample permits slower delivery to maintain an equivalent 100:1 dilution on original exhaust basis which permits longer conditioning.

Some evidence that one or both of these effects influence odor intensity was found in evaluation of exhaust samples trapped at Dry Ice temperature in stainless steel loops packed with clean glass wool. These traps are less efficient than the Chromasorb 102 traps in that some of the more volatile components pass the fiberglass trap. In an odor evaluation of exhaust of the GMC3-53 at no load, 1,000 rpm the direct sampling by the dynamic dilution procedure found 2.9 intensity units while the cold trapped material carried through the syringe method showed 2.0 units. This is a considerably smaller loss than found for the exhaust drawn directly into the syringe. Some of the loss of odor of the cold trapped material may be caused by the inadequate retention of high volatility material in the trap and by incomplete transfer of low volatility material from the trap to the syringe.

The intent of the work in odorant dilution and presentation systems was development of procedures suitable for isolated fractions of diesel exhaust or for synthetic materials representing compound classes known to be present in exhaust. For this purpose it was assumed that if the odor of an exhaust sample was unchanged by the dilution and presentation method from that for exhaust through the dynamic dilution apparatus, then the individual exhaust components would not be lost in sampling and presentation.

Table 14.- Exhaust odor intensity as influenced by sampling method (DI odor units, exhaust dilution 100:1)

(GMC-353 engine)

| Engine mode | Sampling | | |
|---|---|---|---|
| | Direct | Syringe | Delay (4 min) |
| No load, 1,000 RPM | 3.7 | 2.0 | 2.9 |
| Full load, 2,100 RPM | (5.8)[1/] | - | (2.8)[1/] |

1/ Limited data

Table 15.- Efficiencies of reagent scrubbing in removal of test compounds

| Scrubber solution | Test Compounds | | | | | |
|---|---|---|---|---|---|---|
| | Ketene | Ethyl hydro-peroxide | Propylene-oxide | Methyl acrylate | Vinyl propionate | Allyl propionate |
| $H_2O$ | 13 | 92 | 0 | 2 | 15 | 3 |
| $Na_2SO_3$ | 79 | 94 | 5 | 29 | 11 | 1 |
| Morpholine | 89 | nt | 8 | 24 | 8 | 1 |
| Hydroxylamine | 75 | 95 | 5 | 5 | 49 | 5 |

## Unstable and Reactive Odorants

Several reagent scrubbing solutions were examined to determine their selectivity in removal of reactive exhaust components. The sodium sulfite solution has been used in determination of epoxides 9/, alpha,beta unsaturated compounds 10/, and organic hydroperoxides 11/. The morpholine solution and similar secondary amines such as diethanolamine (which was also used in exhaust scrubbing) have been used in determination of alpha,beta unsaturated compounds 12/, epoxides 12/, and carboxylic anhydrides 13/. The reaction with carboxylic anhydrides can be considered as indicating probable reaction with ketenes. Potassium permanganate is quite general in its action as a strong oxidant and probably reacts with most oxygenates and many unsaturated and aromatic hydrocarbons. Hydroxylamine is known best for its reaction with carbonyl compounds but it may also be used for determination for ketenes 14/.

The effectiveness of these reagent solutions in removal of several trial compounds from gas streams is shown in table 15. The values shown are the percent removal of the test compound at 10 minutes scrubbing with the scrubber containing 15 ml water or reagent solution and gas flow of 4.5 liters per minute.

Previous experience with the hydroxylamine scrubber 3/ has shown it to have only a minor effect on diesel exhaust odor when compared with the water scrubbed exhaust. Because of this it is not likely that either ketene or vinyl alcohol derivatives such as vinyl propionate are important diesel odorants.

Since ethyl hydroperoxide was removed from the gas stream by water it is not possible to reach a conclusion on odor contribution through reagent scrubbing for this compound. However, the water solubility of ethyl hydroperoxide should be greater than that of the higher molecular weight aliphatic hydroperoxides. In this case, a reagent such as sodium sulfite would be discriminating for the less water soluble hydroperoxides. Examination of the solutions subsequent to passing ethyl hydroperoxide through them showed that the hydroperoxide could be recovered by extraction from water but not from the sulfite or hydroxylamine solutions. Both of these latter reagents have reducing action and sodium sulfite is known to form alcohols from hydroperoxides 11/.

Methyl acrylate is the representative compound for alpha,beta unsaturated compounds. It is evident that both the sulfite and morpholine have a low level of effectiveness in removal of this compound class. However, if this class is a major source of odor, some indication of its presence would be given by use of these reagents. Also, methyl acrylate is one of the less reactive members of this class and other compounds such as those with carbonyl or nitrile groups conjugated to the unsaturated bond should be removed to a greater extent.

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9/J. D. Swan. Anal. Chem., 26, 878 (1954).
10/F. E. Critchfield and J. B. Johnson. Anal. Chem., 28, 73 (1956).
11/A. G. Davies. "Organic Peroxides," Butterworth & Co., London, 1961, pp. 189-191.
12/F. E. Critchfield, G. L. Funk, and J. B. Johnson. Anal. Chem., 28, 76 (1956).
13/J. B. Johnson and G. L. Funk. Anal. Chem., 27, 1464 (1955).
14/W. M. Diggle and J. C. Gage. Analyst, 78, 473 (1953).

Contrary to literature indications, none of the reagents are useful in removing epoxides. Allyl propionate represents compounds with isolated unsaturation and it was not expected that sulfite and morpholine would react with it.

The other approach used in demonstration of the presence of reactive and unstable odorants was carried out by aging the exhaust. Since the exhaust was aged by only four minutes this method was capable of indicating only the most unstable and reactive classes of compounds. Within this time period ketene might be hydrolysed 15/ and hydroperoxides might react with nitric oxide 16/. Other reactions such as rearrangements of strained compounds might occur.

Results of odor measurements on scrubbed exhaust are given in table 16 and on aged exhaust are given in table 14. None of the reagents were highly effective in reduction of odor although permanganate was fairly effective on exhaust of the GM3-53 engine. Permanganate is not specific in its reactions and it is difficult to interpret its effect on odor. The effects of morpholine and sulfite were rather variable and not very large and the exhaust of the GM3-53 engine appeared to be more susceptible to these reagents than exhaust of the Cummins NH-250 engine. Since both the effect on odor and the behavior towards the trial compounds was similar for these two reagents, it is not possible to reach any conclusions on the nature of the odorants. However, both are consistent with the interpretation that some of the odorants are alpha,beta unsaturated compounds. Many of the hydroperoxides may be removed by water scrubbing. Part of the odor removed by water scrubbing has been accounted for in carbonyls, phenols, and hydrocarbons 1/ and it is possible that some of the odor not accounted for may be hydroperoxides.

The reduction in odor by aging of the exhaust (table 14) is greater than that found in reagent scrubbing. No specific class of compounds can be identified by this procedure but odorants disappearing may include those sensitive to oxygen or nitrogen oxides or those subject to internal rearrangement. These types of compounds would probably not be affected by the reagents used.

The loss of odor on aging suggests several problems. One is that it may not be possible to isolate and identify these odorants by methods currently used. Another is the comparability of exhaust odor measurements made under methods of dynamic dilution and of odor chamber or room dilution. Related to this is the ability to account for the total odor as the combined contribution of identified odorants in fresh or stale exhaust. A further problem is the meaningfulness of exhaust odor measurements as made by any individual method in relation to diesel exhaust encountered publicly.

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15/R. N. Lacey. Advances in Organic Chemistry, Methods and Results, v. II, (ed. R. A. Raphael, E. C. Taylor, and H. Wynberg), Interscience Pub. Inc., New York, 1960, pp. 216.

16/D. Gray, E. Lissi, and J. Heicklen. J. Phys. Chem., 76, 1919 (1972).

TABLE 16. - Effects of selective chemical reagents on exhaust odor intensity (DI odor units, exhaust dilution 100:1)

| Exhaust treatment scrubber solution 1/ | GM 3-53 engine | | | Cummins NH-250 engine | | |
|---|---|---|---|---|---|---|
| | No load | Half load | Full load | No load | Half load | Full load |
| $H_2O$ | 3.1 | 2.8 | 5.2 | 4.2 | 2.7 | 3.8 |
| Morpholine | 2.6 | 2.5 | 4.8 | 4.1 | 1.8 | 3.6 |
| Sodium sulfite | 2.6 | 3.2 | 4.6 | 3.6 | 2.6 | 3.7 |
| Permanganate | 2.1 | 2.2 | 3.1 | 2.8 | 3.2 | 3.7 |

1/ All solutions were tested at 0° C, 15 ml in a liquid lift scrubber. Exhaust flow was 4.5 liter per minute. Solution composition specified in experimental section.

## Analytical Methods Development

Organic hydroperoxides are known to be important combustion products 17/ although their instability can make analysis difficult. Some have been shown to be intensely irritating to the nose and to be powerful vesicants 18/. This suggests that they may be detected at low concentrations as part of the diesel odor. The original interpretation of the effectiveness of the sulfite reagent scrubber was that its primary action was removal of hydroperoxides or other oxidizing compounds. Later it was recognized that it might also remove alpha,beta unsaturated compounds but this did not eliminate the possibility that it might also be acting on oxidizing odorants.

Some preliminary work was begun in isolation and analysis of hydroperoxides. The all-glass packed columns appeared to be satisfactory for aliphatic hydroperoxides but not for benzyl hydroperoxide. However, at the termination of this project promising results were being obtained in chromatography of benzyl hydroperoxide with a short glass capillary column and it is probable that this could be developed to give satisfactory results with both the aliphatic and aromatic compounds. A single exhaust sample collected in a cold water scrubber was extracted and processed to show trace amounts of the aliphatic hydroperoxides that had been examined as pure compounds. No quantitative determination was attempted on this sample.

At the stage to which this study had progressed, the major problem was the evaluation of the hydroperoxide collection method over a range of molecular weights and classes of compounds and determination of losses during isolation and processing. Following this, it is likely that the whole procedure could be systematized to permit quantitative exhaust analysis and collection of samples for odor evaluation.

## SUMMARY

Three main accomplishments may be noted for the program carried out during the year of this report. They are:

1. Development of procedures and equipment for evaluation of odorants isolated from diesel exhaust or formed synthetically.

   The need for this method developed in the processing of small isolated samples. The dynamic blending method, used in previous work, was suitable only for large volume continuously generated samples. Experience gained in conversion of a photochemical chamber to use in exhaust odor rating showed the difficulties that may be encountered in alteration of odor and presence of background odor. In particular, it showed the need for regular

17/A. Fish. Angew. Chem. Intern. Ed., 7, 45 (1968).
18/S. Dykstra and H. S. Mosher. J. Amer. Chem. Soc., 79, 3475 (1957).

background odor measurements. The bag dilution system proved to be adequate for use with materials that were not strongly absorbed on the bag walls. However, there was a serious loss of odor from exhaust samples in the bag. The syringe dilution and presentation method was the most satisfactory procedure since it showed the least loss of exhaust odor and presented no background odor problem. Odor loss in the syringe was sufficient to present some problem with quantitative odor assessment, but it should be possible to evaluate unstable and reactive materials when allowance is made for these losses.

2. Demonstration of the existence of unstable and reactive diesel odorants.

   Past studies on the detailed composition of diesel odorants has concentrated on compound classes that are stable in ordinary collection and isolation processes. However, common experience with diesel exhaust odor has indicated that it is unstable. In addition, combustion products are known to include several classes of unstable and chemically reactive compounds. Reagent scrubbing of exhaust showed possible presence of several such classes, including particularly hydroperoxides and alpha,beta unsaturated compounds. Simple aging of exhaust also showed odor change.

3. Initial development of analysis and isolation methods for organic hydroperoxides.

   Work was begun in analysis of those compound classes indicated as chemically reactive odorants. Demonstration of suitable gas chromatographic procedures for hydroperoxides was accomplished.